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पुस्तक पर किसी प्रकार का निशान लगाना वर्जित है। कृपया १५ दिन से अधिक समय तक पुस्तक अपने पास न रखें।

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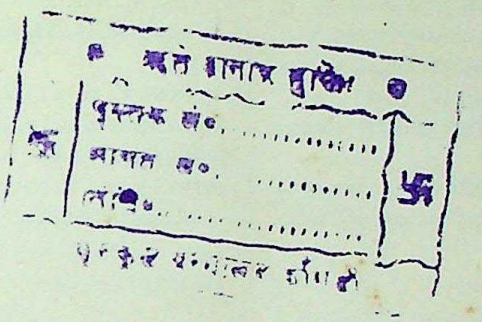

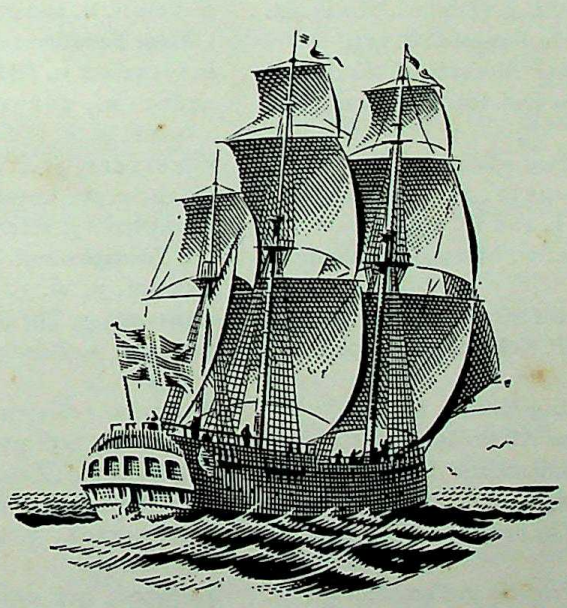

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Assistant Editor W. A. OSMAN, B.Sc., M.Sc., A.R.C.S.

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The IQSY in retrospect

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In his book '*Tractatus physicam astrorum notitiam ex principiis mechanicae proponens*', published in Vienna in 1764, Jacob Wernischek wrote 'Rarely does it happen that the sun is completely free from spots.' This almost certainly understates the case; nevertheless, the world's scientists decided to organize, exactly 200 years later, a two-year enterprise—'The International Years of the Quiet Sun' (IQSY)—confident that at some time in the two-year period 1st January 1964 to 31st December 1965 the Sun would be fairly free of spots. Activity on the Sun reached a minimum during the months of September and October 1964; this was the eighteenth occasion on which it has been 'quiet' since Wernischek wrote the phrase quoted above.

Sunspots had, of course, been observed many centuries earlier. Records of the observations of spots on the surface of the Sun are to be found in the annals of ancient China; Galileo, in 1611, turned his newly invented telescope to examine the solar surface and rediscovered these dark sunspot areas, but did not detect any regular yearly variation in the number of spots. This variation remained undiscovered for a further 200 years. Between 1825 and 1843, a German apothecary, Charles Schwabe, carefully observed the solar surface daily, using a two-inch telescope, and concluded that the sunspots showed a clear 11-year cycle. Since then, it has been found that the numbers of spots build up to a maximum in a period of about four to five years and die away more slowly over a period of six to seven years. Furthermore, although the average 'sunspot cycle' is about 11·1 years, the lengths of individual cycles may be as short as 7 years or as long as 17 years.

It was natural that as soon as the regular variation in the degree of sunspottedness had been observed, attempts would be made to seek some connections between terrestrial phenomena and the sunspot cycle. Even in the last century, there was quite conclusive evidence connecting sunspots with the Earth's magnetism and auroral activity, and there was thought to be a connection with atmospheric temperature, hail, cloud, and thunderstorms (and even the annual quality and quantity of Prussian wines). From time to time, claims continue to be made for the dependence of a wide variety of terrestrial phenomena on the solar cycle. Although there is little interest in some of the more fanciful claims, the interest in those terrestrial phenomena that are unmistakably dependent on solar activity has vastly increased. The world-wide co-ordinated geophysical studies of the last two years were motivated by the desire to know more about this dependence.

Although the extent, if any, to which phenomena in the lower atmosphere of the Earth are affected by the solar cycle is not yet clear, it is now well established that the Earth's atmosphere above altitudes of about 50 kilometres (30 miles) shows a quite significant dependence on sunspots. The Sun emits radiation of a very wide spectral range: for the high atmosphere of the Earth, the important solar radiations are those in the ultraviolet region and the X-region. In addition, it is now known that the Sun emits a continuous stream of electrically charged particles, and that from time to time this stream is supplemented by very intense outbursts from particular regions of the solar surface. These streams of protons and electrons—the 'solar wind'—are mainly responsible for the storm effects that are observed in the Earth's upper atmosphere and in its magnetic field. Although there seems to be no measurable long-term change in the intensity of solar radiation at wavelengths in the visible parts of the solar spectrum, studies of the ionosphere and of the Earth's magnetic field have shown that the intensities of the ultraviolet and X-ray emissions, and the strength of the 'solar wind', change markedly during the solar cycle.

The observational period of the IQSY ended on 31st December 1965. It covered a vast co-operative programme of observations in meteorology, geomagnetism, auroral and airglow studies, ionospheric physics, cosmic-ray studies, and solar studies. In most of the IQSY disciplines, the programmes were similar to those carried out under the conditions of solar maximum activity of the IGY, but there were also some new programmes. One minor but interesting new study concerned a possible interaction between the solar wind and the tails of comets. Comet tails consist of fine particles, and it was suggested some years ago that, if there were a significant interaction between the solar wind and comet tails, then changes in the intensity of the solar wind might be recognized from a study of comet tails. Successful studies of the tails were carried out during the IQSY. Many other new IQSY experiments have formed part of the space-research programme. The first artificial earth satellite was launched by the Russians on 4th October 1957, during the IGY: since then, the number of orbiting vehicles has increased considerably, and so has the sophistication of the scientific experiments and the complexity of the equipment carried in the vehicles. In the IGY, rocket and satellite experiments formed only a very small, but highly important, part of the overall programme; during the IQSY, research with space vehicles formed a major part. Two typical satellite experiments may be mentioned here. The satellite Alouette, constructed by Canadian scientists and launched by the United States, operated throughout the IQSY and provided several hundreds of thousands of records of conditions in the upper regions of the ionosphere, at levels inaccessible to radio-sounding from the ground. A second satellite experiment marked a new step forward in studies of solar activity. For centuries our only way of assessing the progress of the solar cycle has been to count the sunspots, but during the IQSY, the day to day variation in the solar radiation at X-ray wavelengths was studied in a satellite experiment; for the first time ever, scientists could observe the intensity of solar X-rays as it went through a minimum.

The IQSY was the fourth in the series of world-wide co-operative geophysical projects that began with the First International Polar Year of 1882, but the magnitude of the IQSY was, of course, incomparably greater than that of the 1882 venture. At an assembly of participating countries held in Madrid last March, it was stated that more than 71 nations were co-operating, including all those which took part in the IGY. More than 2000 observing stations, and some tens of thousands of scientific workers, were involved in the project. The close co-operation which has been established in recent years between leading scientists of 70 nations should be maintained and extended. The fruits of such co-operation, it is hoped, will appear not only in the immediate field of geophysical science but in the wider field of international understanding and good will.

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Macroscopic quantum effects in liquid helium

W. F. Vinen

Quanta of energy are so small in size, and the permissible energy-levels so numerous, that macroscopic mechanical experiments normally do not show any effects explicable only by quantum mechanics. This article shows that there are conditions in which a substantial proportion of the atoms in a macroscopic quantity of liquid might be in the same quantum state; and it describes a macroscopic mechanical experiment in which the consequences of this effect are directly observed.

Normally, we consider that quantum effects are evident only on a sub-microscopic scale, and that classical mechanics is adequate for the description of macroscopic motion. It is worth while to consider why this is so, and whether there can be any special circumstances in which quantization of, for example, angular momenta can be apparent in a macroscopic mechanical experiment.

Let us look at some macroscopic systems. Consider first a freely moving solid body, which will consist of an assembly of atoms that are more or less rigidly joined together. We know from quantum theory that the angular momenta of the individual atoms about any axis in such a system are not quantized. All that is quantized is the total angular momentum of the whole body, and then only in units of $\hbar$, where $\hbar$ is Planck's constant divided by 2π; the magnitude of $\hbar$ is only of the order of 10^{-27} g cm^2 s^{-1}, so that there could be no macroscopically observable effect.

Let us instead, therefore, consider a case where the orbital angular momentum of each atom or molecule does remain quantized, namely the case of a volume of ideal gas, where there is no interaction between the individual atoms or molecules. We may imagine for simplicity that the gas is contained in a narrow annular region formed between two smooth concentric cylinders. Under normal conditions, the gas molecules will be moving around with random thermal velocities, and the angular momenta of the molecules about the axis of the cylinders will be arranged in the Maxwell-Boltzmann distribution shown schematically in figure 1. The form of this distribution is such that the probability of finding a particle with energy ε is $Ae^{-\varepsilon/kT}$, where A is a normalization constant, k is Boltzmann's constant, and T is the absolute temperature. If the cylinders are at rest, the distribution will be centred on zero angular momentum; if they rotate with angular velocity Ω, it will be centred on an angular momentum $mR^2\Omega$, where m is the mass of a molecule and R is the radius of the annular region. The width of the distribution always covers a range of energies of order kT. Now suppose that the angular momenta of the molecules were not quantized; then it is clear that, as Ω is increased, the total angular momentum of the gas will increase steadily and will correspond to that for a solid body rotating with angular velocity Ω. In fact they are quantized, but it is clear from figure 1 that this will make little difference provided that the spacing between the quantum levels is much less than kT. In normal circumstances this condition is amply satisfied, and we conclude that quantum effects will not normally be observable in the flow of our gas.

However, suppose that it were possible to reduce the temperature of the gas to an extremely low value, so that the quantum-level spacing becomes large compared with the width of the Maxwell-Boltzmann distribution (figure 2). Most of the molecules will now be concentrated in a single quantum state. As Ω is slowly increased (that is, as the distribution curve is shifted), the molecules will tend to stay in this state, until Ω has increased sufficiently for them to tend to transfer completely to the adjacent state. Thus there will be a strong tendency for all the molecules to have the same angular momentum, and for the total angular momentum of the complete system to be quantized in units of $N\hbar$, where N is the total number of molecules. The quantity $N\hbar$, as opposed to $\hbar$, is comparatively large, and might be macroscopically observable. It should be emphasized that, in this case, the total angular momentum is not quantized in units of $N\hbar$ in the sense that other values are not allowed; clearly any value is allowed subject to the total angular momentum being quantized in units of $\hbar$. The point is only that

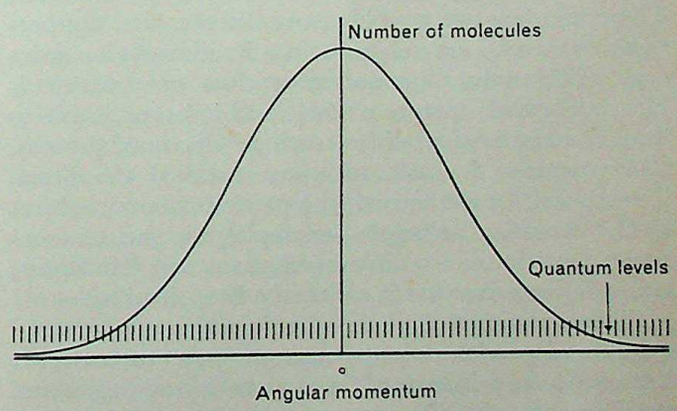

Figure 1 Maxwell-Boltzmann distribution at a high temperature.

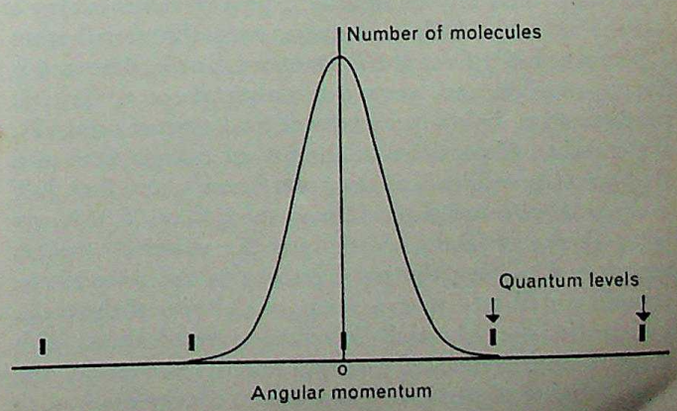

Figure 2 Maxwell-Boltzmann distribution at a low temperature.

W. F. Vinen, *M.A., Ph.D.*
Was born in Watford, England, in 1930 and was educated at Watford Grammar School and Clare College, Cambridge. From 1955, he was a Research Fellow, and then Demonstrator, at the University of Cambridge; he has been Professor of Physics at the University of Birmingham since 1962. His main research interests are in low-temperature physics and solid-state physics.

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if the system is in thermal equilibrium (that is, if the appropriate free energy is at a minimum) there is a strong tendency for all molecules to be in the same angular momentum state, and so for the total angular momentum to be an integral multiple of $N\hbar$. This is the kind of effect we might hope to observe in practice.

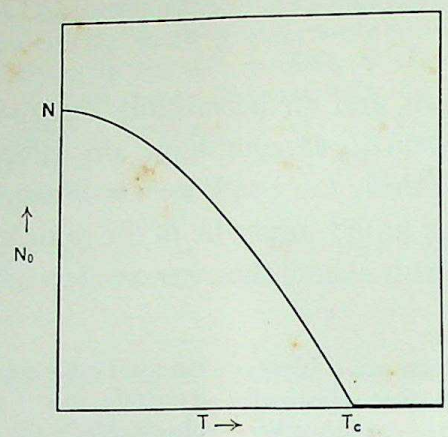

Figure 3 The ideal Bose gas. Number of molecules in the lowest quantum level plotted as a function of temperature.

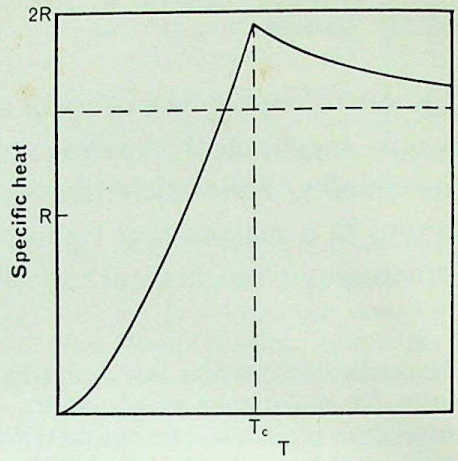

Figure 4 The ideal Bose gas. Specific heat at constant volume plotted as a function of temperature.

The ideal Bose gas

If we calculate the temperature that is required to reduce the width of the Maxwell-Boltzmann distribution to less than the quantum-level spacing, we find that it must be less than about $\hbar^2/(2mkL^2)$, where L is the circumference of the annular channel. If we take L to be 1 cm, we find a temperature of about 10^{-14}°K. With present experimental techniques such a temperature is totally inaccessible, so that the situation looks discouraging.

However, the picture we have been presenting is not completely accurate. It was based on the Maxwell-Boltzmann distribution, which is obtained by a statistical analysis in which it is assumed that the molecules in the system are distinguishable from one another. In fact they are fundamentally indistinguishable. It turns out that this makes no significant difference in the present context, if the temperature is high; there are then so many accessible quantum levels that the probability that any single quantum level is occupied is much less than unity. But if the temperature is not high, the Maxwell-Boltzmann distribution has to be modified. There are then two possible cases. In the first, the particles concerned are subject to the Pauli exclusion principle. This states that not more than one particle is allowed in each quantum state, and it is applicable to most fundamental particles, such as electrons, protons, and neutrons; it leads to what is called the Fermi distribution. In the second, the particles are not subject to the exclusion principle—examples are various composite particles such as hydrogen atoms and ^{4}He atoms; this case leads to what is called the Bose distribution.

Since we wish to find a system in which a substantial number of particles occupy a single quantum state, we are clearly not interested in systems containing Fermi particles, and therefore we need consider only the Bose distribution. The form of this Bose distribution is such that the probability of finding a particle with energy ε is $1/(Ae^{\varepsilon/kT}-1)$. At low temperatures, this distribution differs markedly from the Boltzmann distribution, and it has a strange and very interesting property [1]. It predicts that, below a certain critical temperature, T_c, the number of particles in the lowest energy level in a Bose gas rises suddenly as shown in figure 3, and that, if N is the total number of particles in the system, T_c is larger by a factor of about $N^{2/3}$ than the value $\hbar^2/(2mkL^2)$ mentioned earlier; the particles not in the lowest level remain distributed over a range of energies of the order kT, as in the Maxwell-Boltzmann distribution. This sudden appearance of an appreciable fraction of the total number of particles in the lowest energy level, at an unexpectedly high temperature, is known as the Bose-Einstein condensation, and it is accompanied by an anomaly in the specific heat of the gas, as shown in figure 4. It is clearly just the kind of effect we want, for if the Bose gas is contained in the rotating annular vessel mentioned earlier, the N_0 condensed particles must always be in the same quantum level (corresponding to the lowest effective energy in the rotating system), and so will contribute a total angular momentum quantized in units of $N_0\hbar$, which could be macroscopically observable.

Liquid helium

Although the factor $N^{2/3}$ does very considerably increase the temperature at which macroscopic occupation of a single quantum level might be expected to occur in our gas, the temperature remains fairly low, and, owing to interactions between the molecules, no real gas remains in the gaseous state at the temperature required. Indeed, with one exception, all known gases would actually have solidified at this temperature, and in these cases there is no hope at all of observing the effect we want.

The exception is helium, which is still liquid at the temperature required, and which indeed remains in this phase down to absolute zero, unless a pressure in excess of 25 atmospheres is applied to it. The common isotope of helium, ^{4}He, is known experimentally to be a Bose particle, and one is therefore tempted to enquire whether any form of Bose-Einstein condensation might occur in real liquid helium as well as in the hypothetical ideal Bose gas.

A strong indication that it does indeed occur is provided by some of the properties of liquid helium that were observed many years ago [2]. At normal atmospheric pressure helium liquefies at 4·2°K, but at 2·19°K it undergoes another phase transition, called the λ-point, marked by a large peak in the specific heat (figure 5). It is obviously tempting to suppose that this anomaly has basically the same origin as that occurring in the ideal Bose gas, and that it therefore marks the beginning of some kind of Bose-Einstein condensation. That this view is probably correct is confirmed by three observations: firstly, the temperature at which Bose-Einstein condensation would be expected in an ideal Bose gas of the same density as liquid helium is quite close to that at which the λ-point appears; secondly, no λ-point occurs

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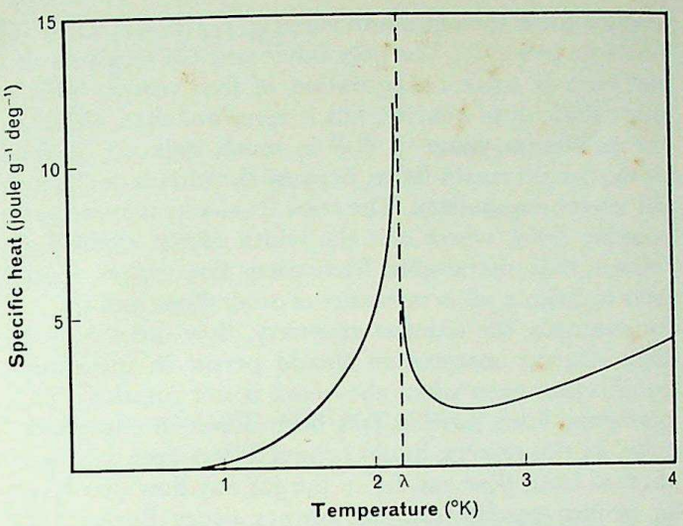

Figure 5 Liquid helium. Specific heat plotted as a function of temperature.

in the liquid phase of the rare light isotope of helium, ^{3}He, the atoms of which are Fermi particles; and thirdly, the properties of liquid helium below the λ-point, where it is called helium II, are quite different from those of any other liquid.

These properties of helium II include what we call superfluidity, and they may be described phenomenologically in terms of a two-fluid model. According to this model, the liquid consists of two interpenetrating fluids: a normal fluid, which behaves like an ordinary viscous liquid, and which carries all the entropy in the helium; and a superfluid, which behaves like an ideal inviscid fluid, and which carries no entropy. In the simplest situations, the two fluids can move relative to one another without frictional interaction. The superfluid density forms a fraction of the total density that varies with temperature, decreasing from unity to zero as the temperature increases from absolute zero to the λ-point. As examples of two-fluid behaviour we may give the following. At low flow-velocities, the viscosity determined by the rate of flow through a narrow channel is zero, corresponding to frictionless flow of the superfluid; on the other hand, the damping of an oscillating disk in the liquid indicates a normal viscosity, corresponding to that of the normal fluid. Thermal conduction can take place by a counterflow of the two fluids, which leads to an extremely large thermal conductivity. In addition, two modes of propagation of longitudinal waves are possible. One corresponds to ordinary sound, in which the two fluids move in phase; and the other is observable as an undamped temperature wave, in which the two fluids move in antiphase.

It is clearly very tempting to identify the superfluid and normal fluid components in the two-fluid model with the condensed and excited particles in the ideal Bose gas. As we shall see in a moment, this idea is rather too naïve, but it does suggest that, in the flow of the superfluid, we might be able to find the macroscopic quantum effects for which we are looking.

We believe now that there are such quantum effects associated with the flow of the superfluid, and that they take the expected form. Thus in the narrow annulus described earlier, the angular momentum of the superfluid is quantized according to the equation $mv_sR = n\hbar$, where v_s is the component of the superfluid velocity round the annulus, and n is an integer. More generally, as is suggested by this equation, rotation of the superfluid is possible only if the velocity falls off inversely as the radius from some axis. This restriction, which does not apply to a normal fluid, means that the flow must take the form of a vortex, and that the circulation associated with this vortex, defined as the line integral of the velocity taken round a circuit that encloses the axis of the vortex, must be quantized in units of h/m. The axis of the vortex may coincide with some solid body, as in the annular geometry, or it may be in the fluid itself, in which case we have a free vortex. At the centre of a free vortex, there will be a cylindrical hole in the liquid, the size of which is probably determined by a balance between surface-tension forces and centrifugal forces; in a single-quantum vortex the radius of this hole is only of order 1 Å.

An important consequence of these ideas is that when liquid helium, for example, is contained in a uniformly rotating vessel the superfluid cannot rotate like an ordinary fluid. The best it can do is to have in it a uniform array of free vortices, each representing a single quantum. The flow pattern on any scale that is large compared with the vortex spacing (0·2 mm at an angular velocity of 1 rad sec^{-1}) is then closely similar to that of an ordinary uniformly rotating fluid, but the pattern on a smaller scale is very different.

Before we describe some experimental evidence that these ideas are correct, we must give a brief outline of the modern theory of liquid helium [3]. Clearly liquid helium cannot behave exactly like an ideal Bose gas, since the interactions between atoms are much too strong. But similarities do exist, which we may describe by imagining that we start with an ideal Bose gas with the same density as liquid helium and then gradually turn on the appropriate interactions. As we have seen, if the ideal gas is at absolute zero of temperature, all the particles are in the same single-particle energy level, which we shall call the condensate level; if the gas as a whole is at rest, this level will correspond to zero momentum, while if the gas is moving, it will correspond to some finite momentum. The effect of the interactions will clearly be to cause the particles to scatter against one another, and therefore to be scattered out of the condensate level. However, it turns out that, in the present context, this scattering does not have a serious effect; and this is for two reasons. First, the depletion of the condensate level is not complete, in that a fraction of the original population of the level remains in it; this fraction may be small (perhaps only a few per cent), but the population of the level remains macroscopically significant and much larger than that of any other level. Secondly, the scattering is symmetrical, in the sense that particles are scattered out of the condensate in pairs with equal and opposite momenta relative to the momentum of a particle in the condensate. Thus the condensate level remains well defined, and as far as the total momentum of the system is concerned all the particles remain 'locked' to this level, whether or not they actually belong to it. It is for this reason that flow states in helium exhibit macroscopic quantization.

In the ideal Bose gas at a very low but finite temperature, some of the particles are thermally excited out of the condensate level; thermally excited states of the gas can therefore be described in terms of a condensate

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together with a number of freely moving particles with the energy-momentum (ε-p) relation appropriate to free particles, that is, $\varepsilon = p^2/2m$, where m is the mass of a particle. In liquid helium, the interactions cause this picture to be changed. At low energies, it is most convenient to consider the thermally excited states not as free particles, but as sound waves which, to a first approximation, are propagated independently of one another. These sound waves are quantized, and they therefore have particle-like properties; the 'particles' are called 'phonons', by analogy with the photons that are associated with electromagnetic waves. Phonons have the energy-momentum relation $\varepsilon = cp$ (where c is the velocity of sound in the liquid), which is very different from that given above for ordinary free particles. At higher energies, the phonon 'excitation' changes to what is called a 'roton', which has yet another energy-momentum relation, $\varepsilon = \Delta + (p - p_0)^2/2\mu$, where Δ, p_0, and μ are constants; the roton is a modified free particle. This particular picture of helium at a low finite temperature is therefore of a 'ground state', which is locked to the condensate level, together with a gas of phonons and rotons moving in this ground state.

This picture leads immediately to an understanding of the 'two-fluid' behaviour of helium II. For if we consider the effect of giving the gas of phonons and rotons a certain drift velocity relative to the condensate level, we can calculate that the total momentum associated with this drift would correspond to that of a mass that is less than the total mass of the liquid. We can, therefore, identify the normal fluid with this gas of phonons and rotons, and what is left over with the superfluid. Thus the properties of the superfluid will be the same as those of helium at the absolute zero, and they will include the macroscopic quantum effects that we have already described. The effective density of phonons and rotons will increase with increasing temperature, and this will be observed as an increasing normal fluid density and decreasing superfluid density. The superfluid density will vanish altogether at the λ-point, as will the macroscopic occupation of the condensate level.

We must refer briefly to the explanation of the fact that, up to a certain critical velocity, the superfluid will flow through a channel without friction. Suppose, for example, that helium at absolute zero is flowing round the annular channel described earlier, and that the walls of the channel are at rest. By what mechanisms can it slow up? Basically there are two: either it can suddenly slow up as a whole, jumping from one state of quantized angular momentum to another; or the energy of the flow can be dissipated by the creation of some localized disturbance. In both cases the process would occur through interaction with the walls of the channel. As L. D. Landau's original paper [3] suggested, the first of these processes is extremely unlikely to occur, for it is difficult to see how a sudden change in the state of the whole liquid can take place as a result of what is only a localized perturbation applied at the walls. The second process is much more likely to occur, but only if the liquid as a whole loses energy when the disturbance is created. It can be shown by straightforward mechanics that, if E is the energy associated with the disturbance and P is its momentum, then this condition is not satisfied unless the velocity of flow exceeds a critical value equal to E/P. The simplest localized disturbances are phonons and rotons, and for these the minimum value of E/P is very large (of order 60 m sec^{-1}). The only other possible localized disturbance is some configuration of free vortex. This is more difficult to analyse, but it turns out that, although the minimum value of E/P is much reduced, it does nevertheless remain finite, because the circulation round the vortex is quantized. The critical velocity is found to be roughly $\hbar/md$, where d is the width of the channel. It follows that metastable frictionless flow states should exist in helium up to velocities of order $\hbar/md$, and that in, for example, the annular geometry, flow states of quite high angular momentum should persist in metastable equilibrium even when the vessel is not rotating. Such persistent flows have in fact been observed experimentally. In this respect, liquid helium differs from the hypothetical ideal Bose gas, for in the gas any flow that is not in proper equilibrium can always decay through the

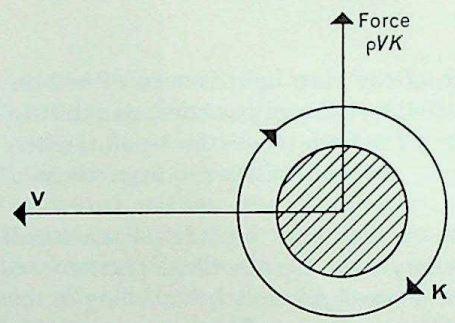

Figure 6 The Magnus effect.

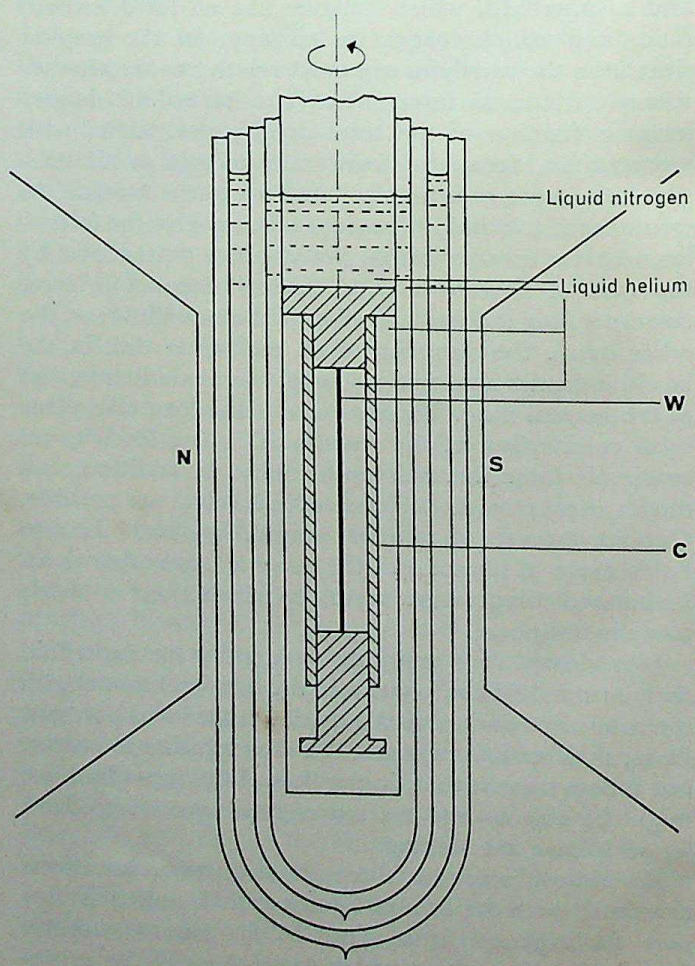

Figure 7 Apparatus, mounted between poles of a magnet, for the detection of single quanta of circulation in liquid helium II.

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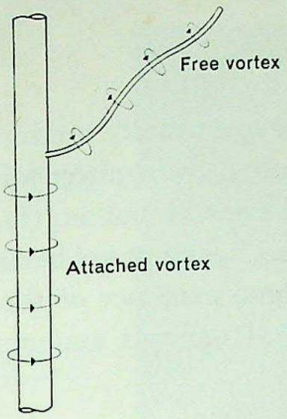

Figure 8 A vortex partly attached to a wire.

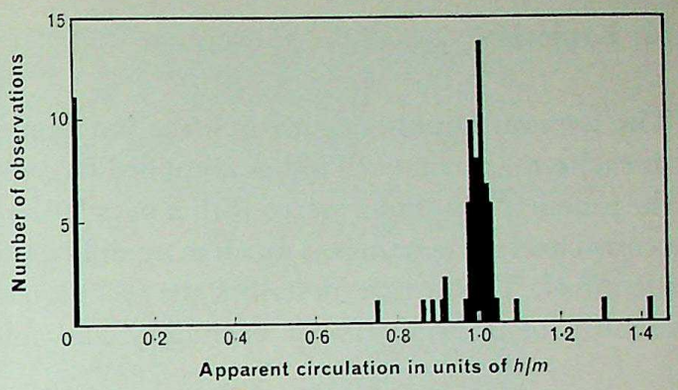

Figure 9 Histogram showing the number of measurements of circulation that were observed to be stable against repeated vibration of the wire with large amplitude.

excitation of single particles out of the condensate, since the form of the ε-p relationship for these particles makes this process always energetically possible.

Experimental evidence

We shall not have space to describe completely the considerable body of experimental evidence that now exists in favour of the ideas that we have been discussing [4]. We shall instead describe just one experiment in which quantization of circulation in the superfluid component of helium II has been observed by direct mechanical means [5].

The experiment is very simple and makes use of the following effect. If a cylinder moves with velocity V in a direction perpendicular to its length through an inviscid fluid, and if there is a circulation of fluid of magnitude K round the cylinder, then the cylinder experiences a transverse force per unit length of magnitude ρVK, where ρ is the density of the fluid (figure 6). This is the Magnus effect, which is well known in classical hydrodynamics, and is responsible for the lift on an aerofoil.

The apparatus for the experiment is shown schematically in figure 7. It consists of a closed cylindrical vessel C, down the centre of which is stretched a fine wire W. The vessel can be filled with helium II at a low temperature, at which the density of the superfluid accounts for most of the total density. The aim of the experiment is to produce a circulation of superfluid round the wire by rotating the apparatus about an axis coincident with the wire, and then to measure this circulation by its effect on the modes of transverse mechanical vibration of the wire. In the absence of any circulation, the wire vibrates in a single fixed plane (at least ideally), but in the presence of a circulation, the Magnus effect will cause this plane to precess. The magnitude of the circulation can be deduced from the measured rate of precession. In practice it is not convenient to make this measurement by direct visual observation; instead the apparatus is placed in a transverse magnetic field, and the vibration can then be observed as an electrical potential induced between the ends of the wire. This potential will alternate, and the amplitude will increase and decrease as the plane of vibration precesses.

When this experiment was first carried out, circulations of the expected order of magnitude were measured, but they were not apparently quantized. However, the reason for this is easy to see. For it is obviously possible to have a situation where a quantized vortex is attached to only a portion of the total length of the wire, a remaining part of the vortex being free (figure 8), and, since the experiment measures only a circulation averaged along the length of the wire, this situation will be observed as a circulation that is not apparently quantized. However, it is also clear that such a situation is likely to be rather unstable. It was therefore decided to try vibrating the wire rather violently for a time, to disturb any metastable equilibria, and then to see whether the apparent circulation had changed. In many cases it had changed, but in some cases it appeared to be quite stable. The values found for these stable circulations are plotted on a histogram in figure 9, and it can be seen that, as was to be expected, there is a marked peak close to the value h/m, corresponding, we believe, to a single-quantum vortex completely attached to the wire. The experiment has very recently been successfully repeated by S. R. Whitmore and W. Zimmerman [6], who find that with wires of larger diameter than those used in the original work stable circulations of $2h/m$ and $3h/m$ can also be observed. It is worth remarking that the observations of figure 9 were actually made after rotation of the apparatus had ceased, so that they represent persistent metastable circulations of the type discussed earlier.

We may recall that superfluid circulation is quantized in liquid helium because the flow is locked to the condensate level, that is, to what is really a single-particle quantum state. Thus in the observations that we have just been describing we are in effect looking at this single-particle quantum state, and we are doing so in an experiment that is macroscopic and purely mechanical.

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Chemical transmission in the central nervous system

K. Krnjević

The nervous impulses that reach the junction of one nerve cell with another are usually unable to excite the second cell unless amplified by a chemical transmitter. The chemical transmitter for the junction of a motor nerve with a muscle has been known for some time to be acetylcholine; the central nervous system is so much more difficult to investigate that its transmitters have not yet been identified. This article describes the techniques of investigation, and gives some evidence of the identity of transmitters for excitatory and inhibitory impulses in the central nervous system.

The nerve cells of the brain and of the spinal cord are independent units. When a cell is excited, it gives rise to a transient electrical impulse, which spreads by a process of self-regeneration over the soma—the cell body—and the branches of its axon as far as the nerve endings. As the axon of some neurons is over a metre long, the nerve impulse may travel in this way for a considerable distance, though remaining within the same unit. However, the nervous message is eventually transmitted to another cell, and one of the more interesting problems of the study of the central nervous system is that of finding out how this is done.

Synapses

The point of contact is called a synapse, and neuronal cell bodies and their dendritic branches are covered with many thousands of these synapses with nerve endings belonging to other cells (figure 6).

The structure of synapses has become clear in recent years largely as a result of the use of the electron microscope (figures 1 and 2). Although various kinds of synapse probably exist, all have one essential feature in common: there is a true discontinuity between the presynaptic nerve ending and the post-synaptic cell. The presynaptic and post-synaptic surface membranes remain distinct, and they are usually separated by a gap of some 20 mμ, the synaptic gap, which must be crossed by the nerve signal. One often sees mitochondria within the ending, and their presence indicates a high level of metabolic activity. There are, in addition, a large number of characteristic bodies, generally known as synaptic vesicles, with a diameter of about 50 mμ.

The nerve endings are usually so small that they cannot generate enough current to excite the post-synaptic cell electrically. It is only at some exceptional synapses, where the presynaptic endings are very large or the synaptic gap is partly absent, that passive electrical spread may be sufficient to product a substantial change in excitability. In most cases, the signal must be amplified through the agency of a chemical transmitter [5].

Transmitters cannot be synthesized without a specific enzyme and a suitable source of energy. The energy is probably supplied by metabolic systems associated with the mitochondria that are present in the nerve endings. The specific enzyme is synthesized in the soma, presumably by the RNA-ribosome mechanism, and carried out into the axon and its various branches by a continuous flow of the internal fluid, the axoplasm (figure 3). Some transmitter is synthesized throughout the axoplasm, but it is probably stored to any important extent only in the nerve endings. Several authors [3] have suggested that the synaptic vesicles (figures 1 and 2) are the sites of storage, but there is still no direct evidence for this hypothesis.

When a nerve impulse reaches the ending, it triggers a transient release of transmitter, either by a direct electrical effect, or by allowing some inflow of Ca^{++} ions into the internal fluid. As soon as the transmitter has produced its effect, it is removed from the synaptic region, through reabsorption into the nerve endings or by enzymatic destruction.

There are other enzymes that are specifically concerned with chemical transmitters, such as enzymes needed for their removal, and these are also synthesized in the cell body and may be found throughout the neuron.

Excitation and inhibition

Different synapses transmit either excitatory or inhibitory signals. Excitatory signals reduce the cell membrane potential until, at a certain threshold level of depolarization, the cell 'fires off' an all-or-none impulse. The synaptic action of a single nerve ending is usually quite small, and the threshold is reached only when several endings

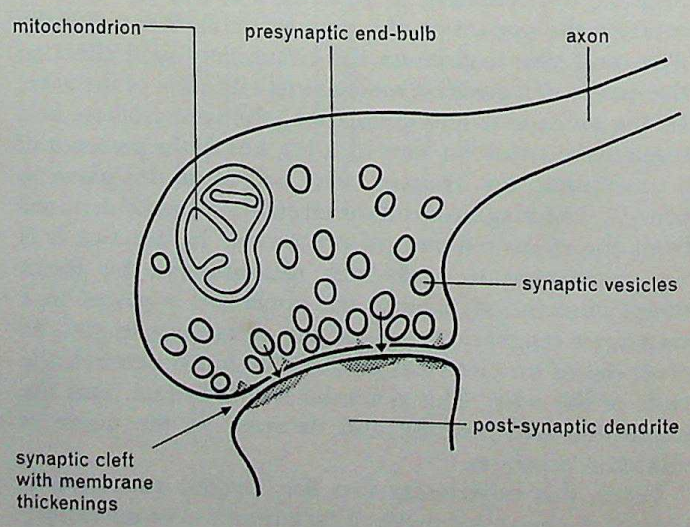

Figure 1 Diagram of a nerve ending with vesicles and part of the post-synaptic cell. The arrows indicate the release of transmitter into the synaptic gap.

K. Krnjević, *M.B., Ch.B., B.Sc., Ph.D.*
Was born in Zagreb in 1927, and was educated at Edinburgh University. He worked for two years in Seattle, at the University of Washington, and for two years in Canberra, at the John Curtin School of Medical Research. His research interest has always been in the physiology of the nervous system. After five years at the Institute of Animal Physiology, Babraham, Cambridge, he is now Wellcome Professor of Research in Anaesthesia at McGill University.

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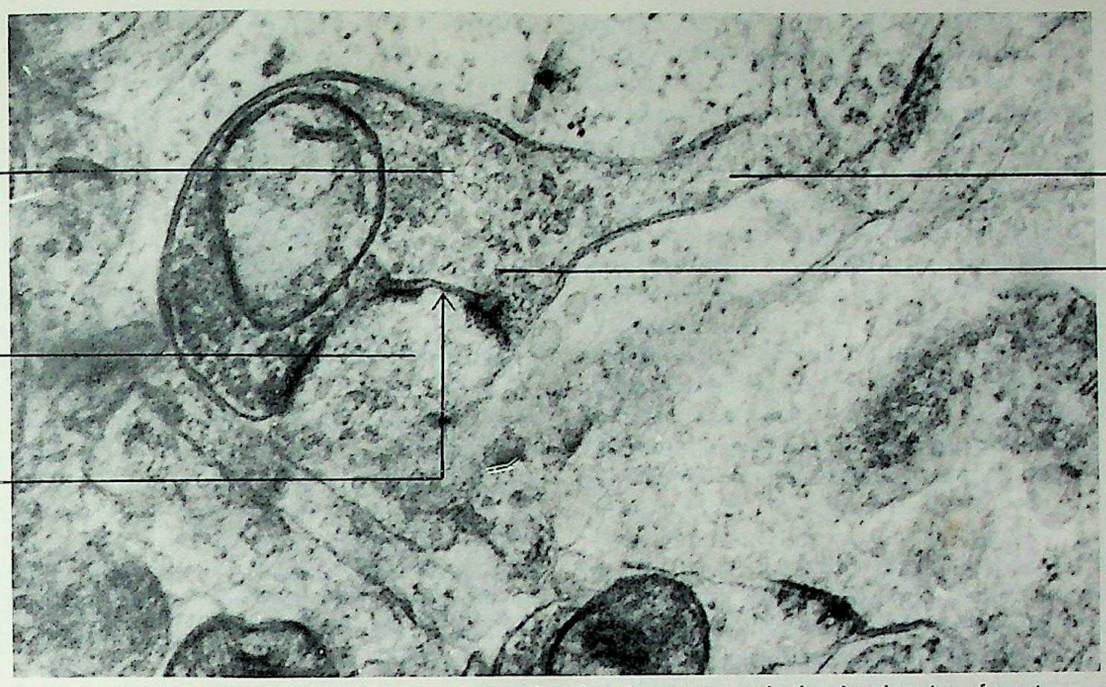

Figure 2 Electron micrograph showing a nerve ending forming synapses in the visual cortex of a cat. Note the synaptic vesicles inside the ending. (×20 000) (By courtesy of Dr M. Colonnier)

discharge at the same time. Inhibitory signals prevent depolarization of the membrane, and therefore neutralize any excitatory effects.

Ions cannot readily pass through the membranes of resting neurons. This is especially true of sodium ions, which have a relatively large effective volume in solution. Potassium and chloride ions penetrate somewhat more easily, and, owing to a difference in ionic composition between the internal and external fluids, they set up a K^+ (or Cl^-) diffusion potential of about 70 mV across the resting membrane. The reaction started by the excitatory transmitter makes the membrane much more permeable to all ions, Na^+ as well as K^+ and Cl^-: in effect, the membrane resistance is short-circuited and the potential across the membrane drops. Initially, the change in potential is graded, depending on the amount of transmitter released by various endings, but if the threshold is reached, the all-or-none impulse is generated and travels through all parts of the post-synaptic neuron.

The inhibitory nerve endings release a different transmitter, which produces an increase in the permeability to small ions, including K^+ and Cl^-. It is as if certain pores appeared in the membrane through which any ion below a certain size could diffuse. The critical size is such that sodium ions still cannot pass, so that the 'resting' character of the membrane, as a K^+ electrode, is further enhanced. The membrane potential is therefore 'clamped' near the resting level, and excitation becomes correspondingly more difficult.

A typical nervous pathway carries impulses that excite some nerve cells and inhibit others. For instance, in the control of movements of the limbs it is essential that a stimulus that causes a flexor reflex, by exciting flexor motoneurons, should at the same time stop any contraction of the opposing muscles, by inhibiting the extensor motoneurons.

So far as we can tell, all the branches of a given neuron release the same substance during activity, and

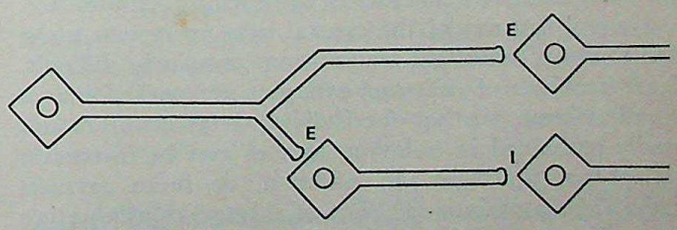

Figure 4 The mechanism of inhibition. All the branches of a given cell release either an excitatory or an inhibitory transmitter. Inhibition therefore requires an additional interneuron. In this diagram, excitatory synapses are marked E and the inhibitory synapse I.

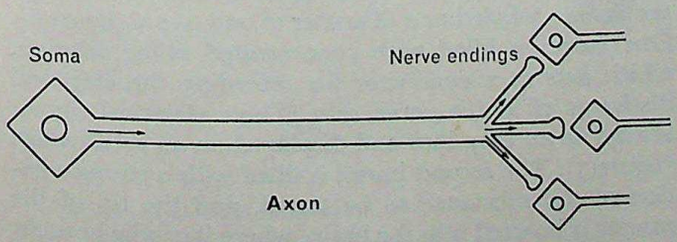

Figure 3 Diagrammatic representation of chemical transmission. The enzyme required for the synthesis of the transmitter is manufactured in the cell body, and then slowly carried into the axon and the various terminal branches by axoplasmic flow. The transmitter is continually being synthesized in the axoplasm, and is probably stored in the endings.

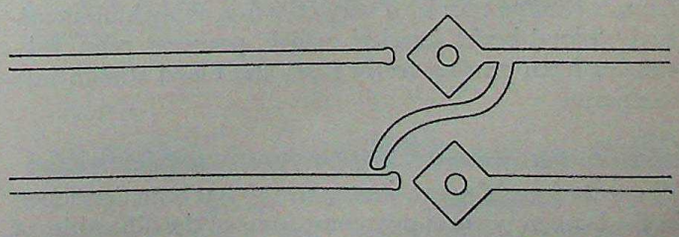

Figure 5 A possible mechanism for presynaptic inhibition. All the synapses are excitatory, but presynaptic depolarization reduces the synaptic potency of the nerve endings in the lower pathway.

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a given substance produces the same effect on all sensitive cells. Any one neuron therefore either excites or inhibits other cells. Inhibitory effects are usually obtained through the action of a special inhibitory interneuron [4]. Such an interneuron is excited by various pathways, and it inhibits other cells by releasing an inhibitory transmitter from all its nerve endings (figure 4).

According to a current theory [5], some nerve fibres activate interneurons that have branches with excitatory endings forming synapses on presynaptic fibres (figure 5). The latter are partly depolarized, and if a volley of impulses reaches them from their own cell bodies at about the same time, they therefore release a smaller quantity of transmitter than usual. The final result is therefore a particular kind of inhibition, known as presynaptic inhibition, produced without an inhibitory transmitter.

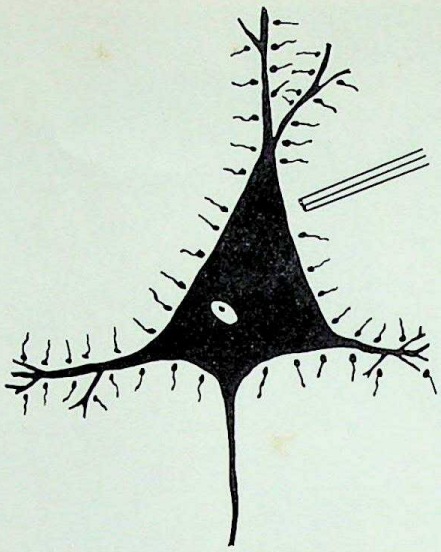

Figure 6 Diagram of micro-iontophoresis. Only the tip of the double-barrelled micropipette is shown. The cell and its dendritic branches are partly covered by numerous nerve endings. (Approximately to scale.)

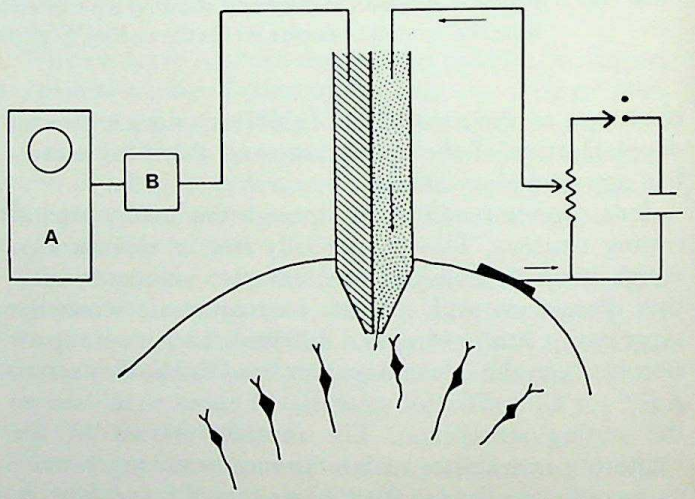

Figure 7 Diagrammatic representation of micro-iontophoresis, with the micropipette grossly out of scale. The left-hand barrel contains a strong salt solution and is connected through an amplifier to the oscilloscope: the neuronal electrical responses are recorded through this channel. The other barrel has been filled with an ionized substance, which is now being carried out of the tip by a small electric current. A= oscilloscope, B= amplifier.

Identification of a chemical transmitter

Before a substance can be accepted as a probable synaptic transmitter, it must fulfil certain criteria. For example, the postulated transmitter must excite or inhibit the relevant neurons. Then, one should be able to demonstrate its presence in the presynaptic neurons, as well as its release during activity. Finally, if the substance has a specific chemical antagonist, this should block synaptic transmission.

We have enough evidence to satisfy all these conditions only for the junction between nerve and skeletal muscle, where acetylcholine (ACh) is almost certainly the normal transmitter. After its release from the motor nerve endings, ACh depolarizes the muscle fibre in the junctional region and is then rapidly destroyed by the hydrolytic enzyme, cholinesterase. The preganglionic fibres of the autonomic nervous system also release ACh, and so do the post-ganglionic parasympathetic fibres. They are all therefore known as cholinergic fibres. In contrast, the sympathetic post-ganglionic fibres probably release noradrenaline, and they have therefore been called adrenergic fibres. For all other kinds of synapses we have much less evidence about the identity of the chemical transmitter.

Several features of the central nervous system make the study of chemical transmitters peculiarly difficult. Vast numbers of cells and synapses are packed into a small volume, so that the individual synapses are not easily examined in isolation, as they can be in certain peripheral junctions. In addition, as brain extracts inevitably contain a mixture of substances originating from different kinds of cells, the functional significance of these substances cannot be determined in any simple way. A further difficulty is that one cannot test possible transmitters by intravascular administration, because the blood supply of the central nervous system is separated from the nerve cells by a very effective, though unidentified, 'blood-brain barrier' which prevents most substances from passing freely from the blood stream into the tissue.

Methods and results

The technique of micro-iontophoresis has been developed in the last ten years to overcome some of the difficulties of investigation. It is based on the well-known fact that, if an electric current is passed through a solution of an electrolyte, positive and negative ions tend to move towards the cathode and the anode respectively.

Double-barrelled micropipettes are prepared by drawing out two glass tubes that have been fused together side by side. The two barrels remain independent, and they have separate openings at the tip, even though the tip as a whole has a diameter of only 1–2 μ (figure 6). One barrel is filled with concentrated saline solution, which acts as a conductor for recording the electrical discharge of active nerve cells. These electrical signals are led to an amplifier and displayed on an oscilloscope (figure 7). The second barrel is filled with a strong solution of the substance to be tested, and the tip of the pipette is inserted into the brain, where it can be brought extremely close to an individual cell without injuring it (figure 6). If the substance forms ions in solution, as do most of the substances of interest, these are easily released from the tip by passing a minute current through the barrel (figure 7).

For instance, if ACh is to be tested, the barrel is filled

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with 1M AChCl. The solution is made a little positive relative to the brain, and a current of ACh ions then flows out of the tip. An appreciable concentration of ACh thus builds up in the tissue just outside the tip.

The current required is usually too small to excite or depress the cells by an electrical effect, but if a cell is sensitive to the applied chemical, the resulting change in activity can be detected through the recording barrel. A further elaboration of this technique uses micro-pipettes with three or more barrels; several substances can then be tried out on the same cell. This is particularly useful when studying the interactions of chemical antagonists.

The main advantage of micro-iontophoresis is that only minute amounts of any substance are applied, and that this affects only a tiny area around the neuron under observation. Uncertainty as to the site of action thus becomes very small—probably with a radius of less than 50 μ. A further advantage is that one can imitate the normal release of transmitter from nerve endings by using very brief pulses of iontophoretic current.

Micro-iontophoresis has been used to study the chemical sensitivity of neurons in several parts of the vertebrate central nervous system. The results of these experiments have been summarized in reviews by G. C. Salmoiraghi and F. E. Bloom [10] and by Krnjević [7], and in the *British Medical Bulletin* [1, 2, 8, 9].

One of the most interesting conclusions of this work is that most central neurons are not very much affected by substances, such as ACh, adrenaline, nor-adrenaline, 5-hydroxytryptamine, and histamine, which have a strong action on peripheral nerve and muscle cells. All of these substances have been considered as potential neurotransmitters, but so far only one rather unusual kind of central synapse has been found where one of these compounds (ACh) does almost certainly act as a transmitter. This kind of synapse occurs in the spinal cord at the endings of recurrent branches of motor-nerve fibres. As we have already stated, the motor-nerve fibres activate muscle by releasing ACh: it appears that they also release ACh from their intraspinal branches, which excite certain inhibitory interneurons known as Renshaw cells (figure 8). These cells are extremely sensitive to ACh: a short micro-iontophoretic application of ACh excites them very sharply (figure 9). Further evidence that this is a cholinergic synapse is given by the fact that normal transmission is blocked by the characteristic antagonists of ACh in muscle, such as the paralysing agents tubocurarine and dihydro-β-erythroidine.

On other central neurons, ACh has a different type of action. Unlike the quick excitation seen in figure 9, there is a more gradual change that begins after an appreciable delay; the excitation is relatively prolonged and it substantially outlasts the period of application (figure 10). This type of effect is seen also in smooth muscle of the gut and in some glands, and it is blocked only by substances related to atropine. This slow action of ACh is shown particularly well by certain neurons situated relatively deeply in the cerebral cortex. These cells are surrounded by a network of apparently cholinergic fibres, which probably come from the phylogenetically older regions of the forebrain, the septum and the striatum. The slow action of ACh on cortical neurons is naturally inconsistent with a quick synaptic mechanism, but it could play a significant role in controlling the excitability of the deep cells. The cholinergic network may be part of an ascending activating system through which lower centres of the brain influence the activity of the cerebral cortex.

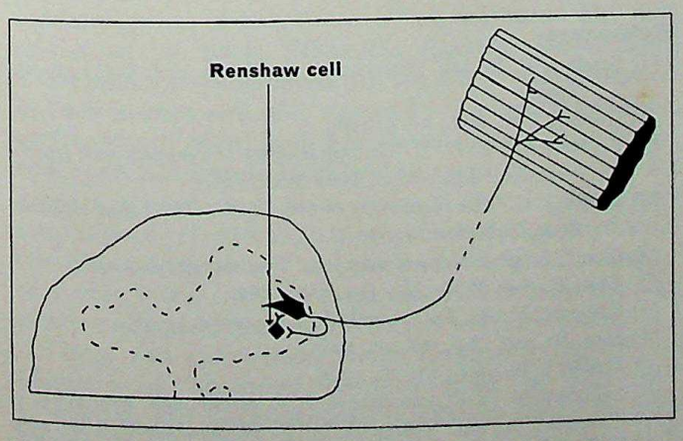

Figure 8 The action of Renshaw cells. A spinal motoneuron, which sends a cholinergic nerve fibre to peripheral muscle, also has recurrent intraspinal branches, forming cholinergic synapses on Renshaw cells. The latter are inhibitory interneurons, which provide a certain amount of negative feedback control over motoneuronal activity

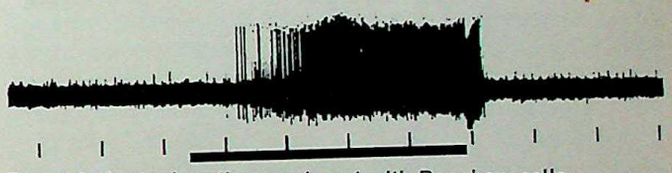

Figure 9 Iontophoretic experiment with Renshaw cells. Vertical lines in upper trace are electrical impulses recorded during the discharge of a Renshaw cell, caused by a short iontophoretic application of ACh. The time of application is indicated by the thick lower line. One-second intervals are also shown.

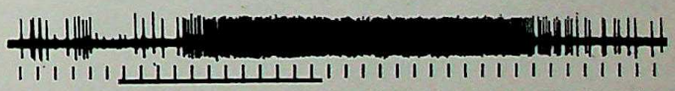

Figure 10 Discharge of cortical cell triggered by a 12-second iontophoretic application of ACh. The cell was firing impulses spontaneously before the micro-iontophoretic release, which is indicated by the lower line. Note the slow and prolonged action. (Time intervals: 1 sec)

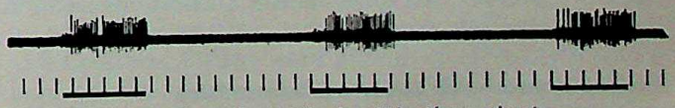

Figure 11 Excitation of a cortical unit by three short applications of L-glutamic acid (indicated by the corresponding lines). Note quick 'on' and 'off' effects, comparable with the action of ACh on a Renshaw cell (figure 9). (Time intervals: 1 sec)

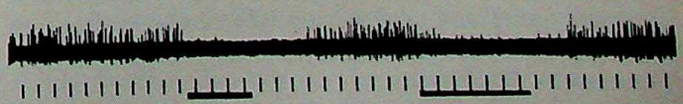

Figure 12 Action of GABA. The spontaneous discharge of this cortical neuron was temporarily inhibited by two short applications of GABA (indicated by lower lines). (Time intervals: 1 sec)

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Figure 13 Forebrain neurons whose strong acetylcholinesterase activity has been demonstrated by Koelle's histochemical method. These neurons are likely to be cholinergic. (×15)

Several other parts of the central nervous system contain cells responding to ACh in a similar slow way. It seems reasonable to suspect that these sensitive cells are not distributed fortuitously, but that they are innervated by cholinergic fibres, which may be part of a diffuse controlling network analogous to the cortical innervation described above.

Other excitatory and inhibitory transmitters

Since the peripheral transmitters do not have a sharp and widespread excitatory action on central neurons, one must look elsewhere for a substance having the properties required of a general excitatory transmitter. The greatest revelation of the micro-iontophoretic studies is perhaps the remarkable potency of glutamic acid. The sharply excitatory action of this amino acid is illustrated in figure 11. There is a remarkable similarity between this effect and that produced on a Renshaw cell by ACh (figure 9).

The central nervous system is richly supplied with glutamic acid, and contains all the enzymes required for both its synthesis and its inactivation. No one has shown conclusively that glutamic acid is released from central nerve endings, and it may be very difficult to do so as long as we have no means of preventing the usual rapid removal of transmitter. The quick ending of the action of glutamic acid (figure 11) shows that, like ACh in muscle, it is immediately destroyed or removed from the site of its action.

A simple process of α-decarboxylation converts glutamic acid to γ-aminobutyric acid (GABA), an extremely potent depressant of central neurons (figure 12). The action of GABA is in many respects what is required of an inhibitory transmitter. As there is plenty of GABA in the brain, this seems to be the only known substance that could be responsible for central inhibition.

There is thus a definite possibility that glutamic acid and GABA are released by the excitatory and inhibitory nerve endings respectively. Until recently, these two substances were thought to be involved only in neuronal metabolism. The idea that they might be synaptic transmitters was rather unexpected, but it should be less surprising now that we have strong evidence that these compounds play a similar role in crustacea [11].

Although we have as yet only fragmentary evidence about the identity of central transmitters, further progress is likely to be quite rapid, as refinements of the methods of analysing the responses of cells make it possible to establish definite criteria by which any postulated transmitters must be examined.

Recent advances in biochemical techniques also promise to throw much light on this problem. For instance, by differential centrifuging one can separate from brain homogenates certain fractions which contain only nerve endings or even only synaptic vesicles. The chemical composition of these structures can then be analysed in detail. Another very promising approach is the histochemical demonstration of different types of neuron in various parts of the central nervous system. One can already detect in this way neurons which are likely to be cholinergic (figure 13) or adrenergic, and it may soon be possible to distinguish neurons with other chemical properties in a similar way.

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English writers on atomism before Dalton

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Douglas McKie

The bicentenary of the birth of John Dalton, who established the modern chemical atomic theory, will be celebrated in this journal later this year. There were English atomists before Dalton, but their theories were based on Greek atomism, and differed fundamentally from his. This article describes the work of two of these atomists and shows the background to Dalton's theories.

During the two centuries preceding the publication of the first volume of Dalton's classic, 'A New System of Chemical Philosophy' (Manchester, 1808–10), there had been two earlier English writers on atomism, Nicholas Hill (*c.* 1570–1610) and Walter Charleton (1619–1707), and there had been much discussion about the atomic nature of matter, notably by Robert Boyle (1627–91) and Isaac Newton (1642–1727). John Dalton (1766–1844), is indisputably the founder of the modern chemical atomic theory, according to which the atoms of the chemical elements are qualitatively different from one another—his English predecessors had taught that the atoms that composed every kind of matter were all qualitatively the same. In this, they followed the revived ideas of the Greek philosophers, Leukippos and Demokritos, transmitted by Epikuros and the Roman poet Lucretius. They held that the differing properties of substances were due to different arrangements in space of various numbers of materially identical atoms. These atoms were considered to differ among themselves in size, shape and heaviness; and to exist in the void—empty space—as minute, solid, indivisible, eternal and indestructible particles. The world consisted of atoms and void, the void, as we might say, being the other half of 'reality'.

Although Dalton was the first to propose a 'modern theory', English atomism before Dalton is of great interest and historical significance. It played its part in infusing into scientific thought in general, and into the expanding science of chemistry in particular, the very useful and readily applied theory of particulate matter.

Nicholas Hill was a Londoner, born about 1570; he was eventually elected a Fellow of St John's College, Oxford, and died in Rotterdam in 1610. He was a Roman Catholic and much interested in theological and philosophical problems, and was the first writer in the modern period of history on Greek atomism. The first edition of his book, *Philosophia Epicurea, Democritiana, Theophrastica proposita simpliciter, non edocta*, was published in Paris in 1601 in Latin; a second edition was published in Geneva in 1619. Both are now very rare. The *Philosophia* was not a large work and its contents were set out in an awkward way, as a series of over five hundred propositions [1]. Although much of it was concerned with the Copernican theory and the problem of the plurality of worlds, it was with this book that Hill became the first modern advocate of the atomic theory of the Greeks.

There was one writer, Pierre Gassend (1592–1655), whose work appeared between those of Hill and Charleton. His *Animadversiones in decimum librum Diogenis Laertii* (Lyons, 1649, 3 vols. folio) included an extensive exposition of the Greek atomic theory, picturing the world as consisting solely of atoms and the void. But in the years between Hill and Gassend, one of the most famous experiments in the history of modern science had been performed in Florence in 1644, an experiment that probably did more than anything else to destroy the dominance of Aristotelian thought in the physical sciences. Evangelista Torricelli (1608–47) showed that when a glass tube, 'two ells long' and sealed at one end, was filled with mercury and then inverted over mercury, the column of liquid descended to a definite level in the tube and left a vacuum at the top of the tube. This demonstrated, after the wearisome philosophical discussion of centuries, that Nature did not 'abhor a vacuum', and thus that one of the two fundamentals of the ancient atomic theory was correct—there could be a void. Gassend made much use of this result in presenting his account of the atomism of the Greeks; and, because of his detailed presentation of their theory, he has often been described as the 'reviver' of the atomic doctrine.

Walter Charleton (figure 1) is a more interesting writer than Nicholas Hill, even if he is far more prolix; he is also a more interesting personality. He was born in 1619 at Shepton Mallet in Somerset, where his father was rector of the parish. He was first educated at home by his father, and at the age of sixteen he entered Magdalen College, Oxford, where, significantly, he came under the influence of John Wilkins (1614–72), who later played a leading part in the assembly of natural philosophers that preceded the foundation of the Royal Society of London in 1660. In 1643, Charleton, aged twenty-four, graduated M.D. in Oxford and was appointed physician to Charles I, who was then in Oxford following the outbreak of the Civil War. After the war, Charleton settled in London in 1650 as a physician. From 1650 until the Restoration in 1660, he published ten books on various topics, including the formation of calculi, anatomy, physiology, nutrition, atheism, the soul, immortality, and Epikuros. Others were published, after the Restoration, on the causes of diseases, on Stonehenge (which Charleton argued had been constructed by the Danes) [2], on wine and the prevention of its putrefaction, on scurvy, and on other subjects. But the most remarkable work of this remarkable man was his *Physiologia Epicuro-Gassendo-Charltoniana: or A Fabric of Science Natural, Upon the Hypothesis of Atoms* etc. (London, 1654), a folio volume of 508 pages. This was the first book on atoms published in England and written in English. It is now very rare.

Charleton was one of the 'Original Fellows' of the Royal Society, signing in Gresham College the well-known declaration of 5th December 1660 for weekly meetings and discussions 'concerning the promoting of Experimentall learning'. He was then living in Russell Street, Covent Garden. In 1676 he was admitted a Fellow of the College of Physicians, of which he was

Douglas McKie, *Ph.D., D.Sc., F.R.I.C., F.R.S.E.*
Was born in 1896. He entered University College, London, in 1920, graduated in chemistry, and was Professor of the History and Philosophy of Science in the University of London from 1957 to 1964. He is now an Emeritus Professor. He has written extensively on the history of chemistry.

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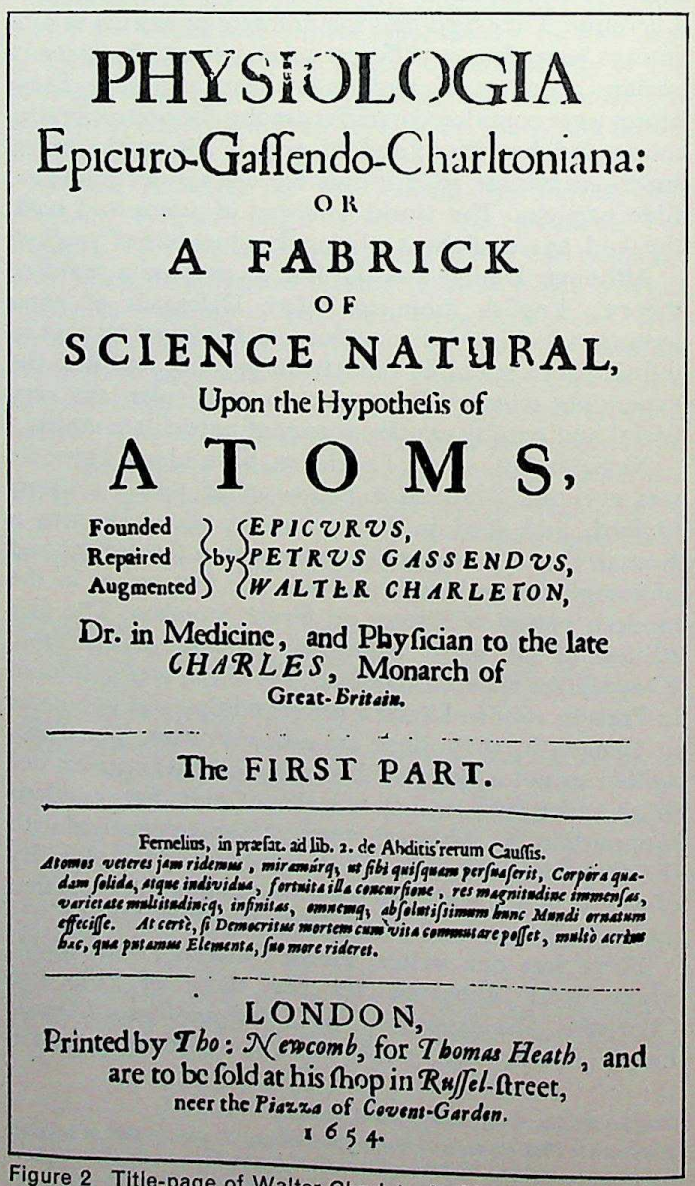
Figure 1 Walter Charleton (1619–1707), M.D., F.R.C.P., F.R.S. Reproduced by courtesy of the Harveian Librarian, Royal College of Physicians of London, from an engraving (not later than 1654) by Lombart in the possession of the College.

President from 1689 to 1691, and Harveian Orator in 1702 and again in 1706. After the execution of Charles I, he was appointed physician to the exiled Charles II; during the interregnum he lived quietly, writing his many books and spending his time in 'the acquisition of science in private', which 'ought to be the principal scope of a wise man'; in these years he was inevitably not in favour with the government, but he so far conformed to the political temper of the times as to use the word 'Monarch' instead of 'King' on the title-page of his *Physiologia*. He died in 1707, leaving many manuscripts.

The *Physiologia* is a large book. Its contents are founded on the doctrine of Epikuros and on the work of Gassend; much of it is actually taken from the pages of Gassend, but it is all composed in Charleton's own analytical, somewhat scholastic and certainly verbose style. He seems to have been influenced in his elaborate argument and refutation by his early association with Wilkins in Oxford. For all that, the book retains its historic importance and interest as the first English work on atoms, although there is little in it that is new. After opening with a classification of philosophers into four general 'Orders' and an account of the principal causes of their dissensions and of the diversity of their sects, Charleton proceeded, as did Hill before him, to write on the much debated question of the plurality of worlds, which he concluded to be 'manifestly repugnant to Authority Divine'. Having passed over these matters fairly quickly, he then dealt with 'Corporeity' and 'Inanity'—matter and void—as the two general 'Parts' of the 'Universe', which, having rejected the plurality of worlds, he contended was our world: 'this World is the Universe'.

Discussion of 'Corporeity' and 'Inanity' led naturally to the subject of vacuum, with the customary lengthy philosophical and logical presentation and criticism of the arguments, for and against, that had persisted through many centuries. Like Gassend, he cited Torricelli's experiment as a powerful demonstration of the ease with which a vacuum could be produced. He added a very striking and interesting diagram of what is now a widely known experiment with the Torricellian tube. In this, the tube is inclined sideways from the vertical, and the mercury rises. It will fill the empty space when the inclination of the tube has brought the upper end of it level with the original height of the mercury. It is said that this convincing experimental demonstration was first made by Blaise Pascal (1623–62) but Charleton's diagram (figure 3) seems to provide the first illustration of it. Charleton's arguments about whether a vacuum was possible were enlivened by a paragraph with the rubric of 'The præcedent Giant-Objection, that Nothing is in a Vacuum; stabb'd, at a blow'. Truly, our modern scientific prose lacks vigour such as this.

In the next part of the *Physiologia*, Charleton expounded



PHYSIOLOGIA
Epicuro-Gassendo-Charltoniana:
OR
A FABRICK
OF
SCIENCE NATURAL,
Upon the Hypothesis of
ATOMS,

Founded, Repaired, Augmented by EPICVRVS, PETRVS GASSENDVS, WALTER CHARLETON,

Dr. in Medicine, and Physician to the late CHARLES, Monarch of Great-Britain.

The FIRST PART.

Fernelius, in præfat. ad lib. 2. de Abditis rerum Caussis.
Atomos veteres jam ridemus, miramúrq; ut sibi quisquam persuaserit, Corpora quædam solida, atque individua, fortuita illa concursione, res magnitudine immensas, varietate multitudinicq; infinitas, omnemq; absolutissimum hunc Mundi ornatum effecisse. At certè, si Democritus mortem cum vita commutare posset, multò acrius hæc, quæ putamus Elementa, suo more rideret.

LONDON,
Printed by *Tho: Newcomb*, for *Thomas Heath*, and are to be sold at his shop in *Russel*-street, neer the *Piazza* of *Covent-Garden*.
1654.

Figure 2 Title-page of Walter Charleton's *Physiologia* (London, 1654).

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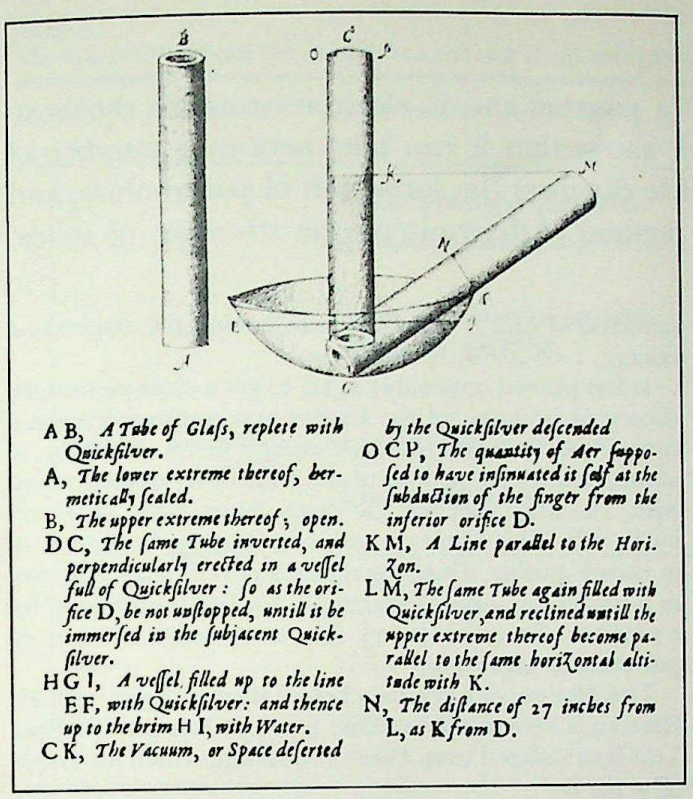
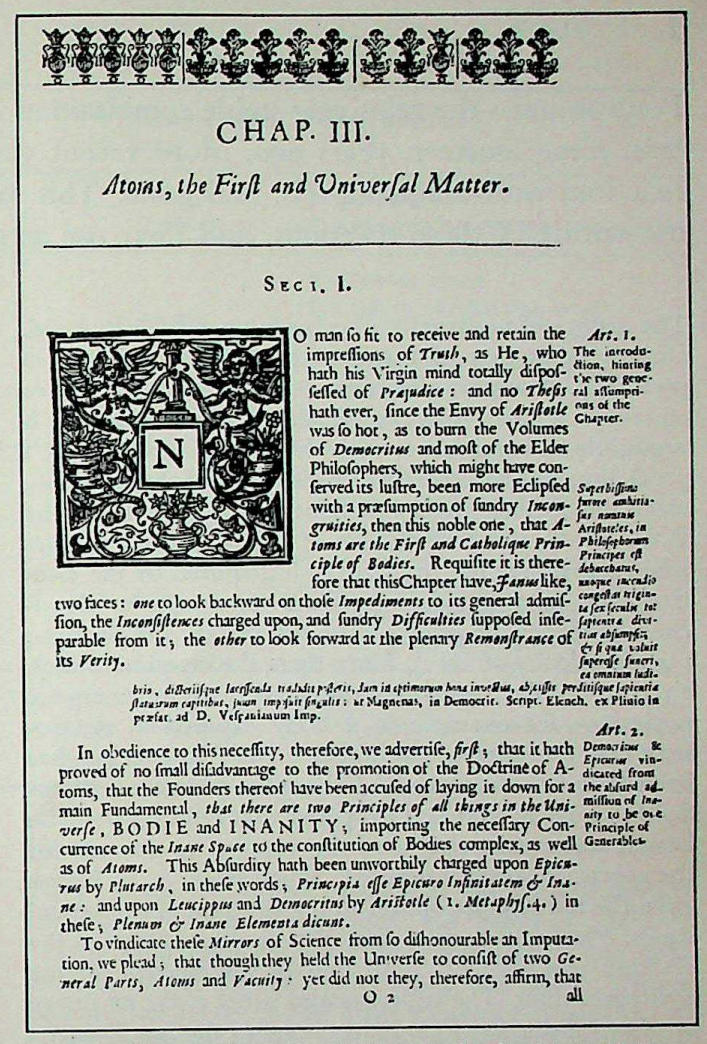


Figure 3 Charleton's diagram of the inclined Torricellian tube.



CHAP. III.

Atoms, the First and Universal Matter.

SECT. I.

NO man so fit to receive and retain the impressions of *Truth*, as He, who hath his Virgin mind totally dispossessed of *Præjudice*: and no *Thesis* hath ever, since the Envy of *Aristotle* was so hot, as to burn the Volumes of *Democritus* and most of the Elder Philosophers, which might have conserved its lustre, been more Eclipsed with a præsumption of sundry *Incongruities*, then this noble one, that *Atoms are the First and Catholique Principle of Bodies*. Requisite it is therefore that this Chapter have, *Janus* like, two faces: *one* to look backward on those *Impediments* to its general admission, the *Inconsistences* charged upon, and sundry *Difficulties* supposed inseparable from it; the *other* to look forward at the plenary *Remonstrance* of its *Verity*.

Art. 1. The introduction, hinting the two general assumptions of the Chapter.

Superbissimus furore ambitiosus nomen Aristoteles, in Philosophorum Principes est debacchatus, usque eò ut omnia congesta triginta sex seculis tot sapientum divitias absumpsit, & si quid voluit superesse furori, ea omnium luditibris, difficilisque lacessendis tradidit posteris, dum in optimarum bona invehitur, abjectis perditisque sapientiæ statuarum capitibus, suum impressit singulis: ut Magnenus, in Democrit. Script. Elench. ex Plinio in præfat. ad D. Vespasianum Imp.

In obedience to this necessity, therefore, we advertise, *first*; that it hath proved of no small disadvantage to the promotion of the Doctrine of Atoms, that the Founders thereof have been accused of laying it down for a main Fundamental, *that there are two Principles of all things in the Universe*, BODIE and INANITY; importing the necessary Concurrence of the *Inane Space* to the constitution of Bodies complex, as well as of *Atoms*. This Absurdity hath been unworthily charged upon *Epicurus* by *Plutarch*, in these words; *Principia esse Epicuro Infinitatem & Inane*: and upon *Leucippus* and *Democritus* by *Aristotle* (1. *Metaphys.* 4.) in these; *Plenum & Inane Elementa dicunt*.

Art. 2. *Democritus* & *Epicurus* vindicated from the absurd admission of *Inanity* to be one Principle of Generables.

To vindicate these *Mirrors* of Science from so dishonourable an Imputation, we plead; that though they held the Universe to consist of two *General Parts*, *Atoms* and *Vacuity*: yet did not they, therefore, affirm, that all

O 2

Figure 4 The opening page of Charleton's chapter on atoms as 'the First and Universal Matter.'

the Greek atomic theory of 'Atoms, the First and Universal Matter' (figure 4). Here he dealt with the evidence for the existence of atoms, showing that there is no infinitely divisible physical continuum in the world; he discussed the essential properties of atoms, their magnitude, shapes, and motions. Following this, he turned to the origin of qualities, that is, of the physical and chemical properties of bodies, to the problems of vision, colour, light, sound, odours and tastes, rarity and density, perspicuity and opacity, and to the whole range of the physical properties of substances. He accounted for all in terms of the ancient theory that had aroused his intellectual enthusiasm and seemed to explain so simply all these complicated matters. As for heat and cold, heat appeared to be a substantial quality produced by 'Atoms of Heat', which by their entry into a body made it hot; cold was similarly a substantial quality, produced by 'Frigorifick Atoms'.

The concluding part of the book dealt with generation and corruption, and with motion. Charleton was now drawing to the end of his long exposition, and in words that reveal his confidence that he had persuaded his readers of the correctness of the arguments he wrote: 'That Nature, or the Common Harmony of the World, is continued by Changes, or the Vicissitudes of Individualls, i.e. the Production of some, and Destruction of other Things, determined to this or that particular species; and that there must be one Catholique Matter, of which all things are Elemented, and into which they may be again, by Dissolution, reduced: are Positions, to which all men most readily prostrate their assent.' He added, that what the primitive matter was, and how it was concreted and in turn reduced was less clear, but in the end he found no great difficulty in these questions.

Such was the earlier atomic theory, as propounded by the ancient Greek philosophers, studied in England by Hill, revived in France by Gassend, and extensively expounded in English by Walter Charleton in his *Physiologia* in 1654. It was the theory used so often for explanatory purposes by Boyle, who, however, was always characteristically 'sceptical' between two differing hypotheses, as René Descartes (1596–1650) had supposed that the finer parts of matter were corpuscles ground down continually in the vortices whirling in the plenum, the continuum of matter, of which the world consisted. Newton, having observed that 'old worn particles' would not produce through ages the same substance with the same properties, dismissed Descartes and did not share Boyle's scepticism, but accepted the ancient theory, as may be seen from many of the queries appended to his *Opticks* [3].

Such also was the atomic theory until Dalton in 1808 took the decisive step of genius in postulating qualitatively different atoms for the different chemical elements.

References

[1] McColley, G. *Ann. Sci.*, 4, 390, 1939.
[2] Charleton's book on Stonehenge, *Chorea Gigantum* (London, 1663; 2nd edn., 1725), is prefixed by what has been described as 'the noblest poem in which English science has been celebrated by an English poet', addressed by John Dryden 'To My Honour'd Friend Dr. Charleton'.
[3] McKie, D. *Phil. Mag.*, 33, 847, 1942.

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Positronium formation and reactions

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J. H. Green

Positronium—the relatively stable combination of a positron and an electron—was first shown to exist some fourteen years ago. More recent work shows that it can take part in a number of reactions with solids, liquids, and gases. This article discusses the formation of positronium and the nature of these reactions, and their use as a method of determining the structure of solids.

The history of positronium begins in 1930 with P. A. M. Dirac's prediction of the existence of the positron—a positively charged electron, e^+. Schrödinger's wave equation applies only to particles whose velocity is negligible in comparison with that of light, and Dirac's prediction was based on his modification of the equation, using the Special Theory of Relativity. The positron, the 'hole' left in the electron sea of negative energy states when energy not less than $2M_0c^2$ is acquired by the electron, was later detected by C. D. Anderson in cloud-chamber experiments (M_0 is the rest mass of the electron: c is the velocity of light). Since then, the creation of such electron-positron pairs by the absorption of energetic radiation—for example in a body exposed to electromagnetic radiation above about 2 MeV in energy—has been found to occur quite frequently. However, it was S .Mohorovićic who first proposed that electron-positron bound states exist and used the concept to account for the spectra of certain nebulae. Much later, A. E. Ruark gave the name positronium to the simplest of the bound states, e^+e^-, and showed that the binding energy of the electron was 6·77 eV (half that of the electron in the hydrogen atom. The experimental proof of the existence of positronium, the foundation stone of the last fourteen years' research, was provided by the ingenious work of M. Deutsch in 1951. This depended on the measurement of the mean life of positrons in a system; the modern method of doing this will be described later. The formation and identification of positronium have already been reviewed in *Endeavour* [4]. The present article deals mainly with its chemistry.

Life history of positrons

The usual laboratory source is the nuclide ^{22}Na, which emits positrons of maximum energy 0·54 MeV in decaying to ^{22}Ne, with a convenient half-life of 2·3 yr. The product ^{22}Ne is formed in an excited energy state and the nucleus goes to its ground level state within 10^{-11} sec, emitting the transition energy as a photon of 1·28 MeV. The emission of this photon almost simultaneously with the positron is one of those instances where Nature has smiled on the experimental scientist and provided him with an unmistakable sign of the 'birth' of the positron. Its 'death' some time later is signalled by the emission of annihilation radiation. A positron-electron pair can be created by supplying an electron with energy equivalent to twice its rest mass—$2M_0c^2$, equivalent to 1·02 MeV: similarly, the annihilation of a pair is announced by the emission of one or more photons having the equivalent energy, 1·02 MeV, between them.

It has proved impossible so far to get a clear picture, in theory or practice, of the history of a positron from the time of its arrival with high energy in an assembly of atoms, molecules, or ions to the time of its passing away with thermal energies (a drop from 0·54 MeV to 0·025 eV). This history is tortuous and can be seen only in broad outline. Thus, the reduction to thermal energies in a simple gas—thermalization—has been considered by a number of authors [1, 2]. Let us consider the fate of positrons in argon gas.

The lifetime of a positron before it annihilates with an electron is known as the Dirac free-annihilation lifetime. This is calculated from Dirac's equation, which for argon ($Z=18$) is

$$p\tau = 2{\cdot}76 \times 10^{-7} \text{ sec atm} \qquad \ldots(1)$$

where τ is the lifetime and p is the gas pressure in atmospheres. In actual fact, the positrons undergo many reactions and this results in a composite lifetime, whose components depend on the various interactions of the positrons. These times have been estimated [2] and are shown in Table 1 as the times taken for a positron to slow down over various energy ranges. In the first range, the positron loses energy very quickly by inelastic collisions that cause ionization and excitation of argon atoms. In argon at one atmosphere pressure, the positron will lose energy from 0·54 MeV to 0·01 MeV in 7×10^{-9} sec. When its energy approaches 15·8 eV, the first ionization energy of an argon atom (E_{ion}), the positron is able to form positronium, the bound state. It can extract an electron from an argon atom and will then form positronium before annihilating later. In fact about 30 per cent of all positrons will do so. Those that do not react in this way lose further energy by collisions and eventually annihilate.

The spins of both the positron and the electron are quantized, and this means that when the particles are close together, their spin axes can be only parallel or anti-parallel. Free annihilation (that is, in a collision between a positron and a free electron) or bound-state annihilation (that is, after forming positronium) will then occur, but in a way determined by the alignment of the spins of the particles. If the spins are parallel, the product is called *ortho*-positronium; it is formed three times as frequently as *para*-positronium and annihilation of *ortho*-positronium is only 1/1120 as frequent as that of *para*-positronium. Using equation (1) we see that, in free space, the lifetimes before annihilation are then 140 nsec for *o*-Ps and 0·125 nsec for *p*-Ps (Ps = positronium; 1 nsec = 1 nanosecond = 10^{-9} sec). These lifetimes are short, but on the other hand they are long compared with the shortest time-intervals that can be experimentally measured, or compared with, say, the vibration time of atoms in

J. H. Green, *M. Sc., Ph.D.*

Was born 1922 at Ipswich, Queensland, and was educated at Ipswich Boys' Grammar School, and the Universities of Queensland and of Cambridge. He has carried out research at these universities and at C.S.I.R.O., Melbourne, and is now Associate Professor at the University of New South Wales. His recent research has been on primary radiation chemical mechanisms; ion formation and ion-molecule reactions in mass spectrometers; positronium formation in gases and liquids; and natural radioactivity.

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Table I
Thermalization of positrons in argon at a pressure of one atmosphere

Stage	Energy (eV)	Slowing-down mechanism	Slowing-down time	Fate of positrons
I (a)		Inelastic collision dominates	$0{\cdot}025\tau_f$* (7 nsec)	1. Slowing down 2. Loss to other processes negligible
	500			
I (b)		Inelastic collision comparable with elastic collision	$< 0{\cdot}32\tau_f$ (90 nsec)	1. Slowing down 2. Loss to annihilation small
	$E_{ion}=15{\cdot}8$			
II				1. Positronium formation 2. Free annihilation 3. Slowing down
	$E_{exc}=11{\cdot}6$			
III		Elastic collision only	$0{\cdot}044\tau_f$ (12 nsec)	1. Positronium formation 2. Free annihilation small 3. Slowing down
	$E_{thr}=9{\cdot}0$			
IV (a)		Elastic collision only	$1{\cdot}0\tau_f$ (276 nsec)	1. Slowing down 2. Compound formation Ae^+ (?) 3. Free annihilation eventually
	0·9			
IV (b)		Elastic collision only	Long	1. Slowing down 2. Compound formation Ae^+ (?) 3. Free annihilation eventually

* τ_f = Dirac free-annihilation lifetime.

a molecule (10^{-14} sec) or the collision time between molecules in a liquid (10^{-10} sec).

Positronium atoms, once formed, can behave in many ways. One of these is to react with substances in the system in which they are produced, and it is reactions of this type that constitute the chemistry of positronium. In these collisions, the ortho-form and the para-form can inter-convert; in addition the atoms lose energy before annihilation in a manner which is not yet understood. Positrons that do not form positronium will also react with the medium, possibly to form positron compounds such as e^+Ar, and will lose energy before eventually annihilating, often well before thermal energies are reached.

Probability of formation of positronium

Figure 1 shows three energy levels for each of the rare gases listed. For argon, the levels are at 15·8 eV, the energy (I) required to remove one electron from the atom; 11·6 eV, the first excitation level (E_{exc}); and 9·0 eV, the 'threshold level' (E_{thr}) for positronium formation in the gas. In the region A, positronium may be formed, but it would dissociate very readily at this comparatively high energy. For positronium to form and be stable after extracting an electron from argon, the positron would need a minimum (threshold) energy of $I-6{\cdot}8$ eV $=9{\cdot}0$ eV. Positrons of all energies between 9·0 eV and 15·8 eV could form positronium, but above 11·6 eV, many positrons would produce only excitation of the argon atom. Thus positronium formation is most probable in the region C, a region known, after its discoverer, as the Ore gap, although it may be formed by positrons with energies in both region B and region C. This means that the chances of positronium formation can be defined only as lying between two limits:

$$\frac{I-(I-6{\cdot}8)}{E_{exc}} > \text{formation probability } (f) > \frac{E_{exc}-(I-6{\cdot}8)}{I}$$

These limits for a few cases, and the experimentally found probabilities of formation, are shown in Table II.

It is what happens now, after positronium has been formed, that is the main concern of this article. This is because the physical and chemical environment determines the interactions and the eventual annihilation mode and time of the quasi-atom. (It will be readily seen that positronium corresponds to a hydrogen radical, with an energy of about 10 eV.) If the positronium is unaffected by its environment, three-quarters will be o-Ps and one-quarter p-Ps, and this ratio will remain the same until annihilation occurs 140 nsec and 0·125 nsec

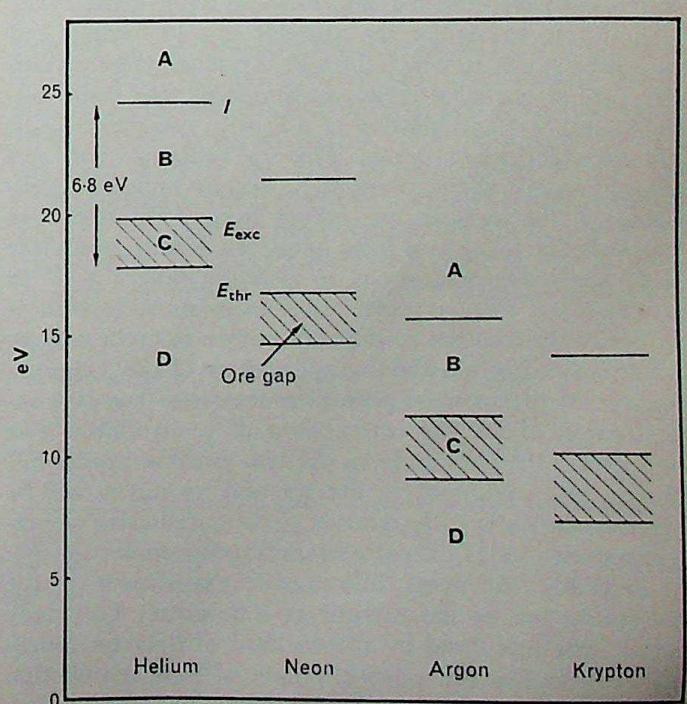

Figure 1 Energy levels and Ore gaps for the rare gases.

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Table II
Energy levels, Ore limits, and percentage of positrons forming Ps as found experimentally

Gas	I (eV)	E_{exc} (eV)	E_{thr} (eV)	Ore limits of f (%)	Experimental f (%)
He	24·6	19·8	17·8	10–28	32±3
Ne	21·4	16·7	14·6	13–32	55±6
Ar	15·8	11·6	9·0	23–43	31±3
					30±3
					27±3
					36±6
Kr	14·1	10·1	7·3	29–48	25

later respectively. This is because, although the energy difference between the two forms is negligible, the transition from one to the other is of a magnetic-dipole character, and therefore spontaneous conversion from one form to another can be ruled out.

However, the conversion of *o*-Ps to *p*-Ps occurs readily in collisions with molecules, and this is referred to as 'quenching'. *p*-Ps is formed to only one-third the extent of *o*-Ps, and its lifetime, 0·125 nsec, is too short for measurement at present. For this reason, most of the work has concentrated on the fate of *o*-Ps—its annihilation lifetime and variations in the number of particles having this lifetime.

Experimental techniques

The formation and interactions of positronium are studied by observing—very conveniently, well away from the system under study—the time between the 'birth' γ-ray (1·28 MeV) and the annihilation γ-rays (⩽0·51 MeV), and the nature of the annihilation radiation itself. This radiation is in the form of three γ-rays if it results from *o*-Ps, and two γ-rays if from *p*-Ps. This means that three scintillation detectors at angles of 120° to one another, coplanar with the positronium chamber, and arranged to record only those signals which arrive simultaneously from the detectors—in triple-coincidence—will give values for the amount of *o*-Ps formed and suggest the way in which the *o*-Ps is quenched by various physical or chemical reactions. Similarly, one could observe the '2γ' annihilation of *p*-Ps with two detectors in double-coincidence array. This 2γ radiation will not always consist of two photons in exactly opposite directions; if the annihilation occurs from *p*-Ps which has appreciable energy, or from positrons which annihilate with the outer electrons of a molecule (about 5 eV in energy), an angular correlation experiment will show a broad distribution round 180° rather than the narrow distribution (within about 2 milliradians of 180°) characteristic of thermalized *p*-Ps. The detectors thus give information about the interactions of positronium. The energies of the photons from the two forms are quite different, and variations in the 2γ and 3γ modes will be displayed clearly if the spectra of the γ-radiation are recorded with a NaI (Tl) scintillation spectrometer [4, 17].

Probably the most informative experiment is the determination of the lifetime of a positron. For many years, this was done by the method of delayed coincidence between the output pulses of two scintillation detectors, one effectively observing the 'birth' γ-ray from ^{22}Na, the other observing the death of the positron by annihilation. The start pulse could by delayed electrically by known times and then combined with the stop pulse in a coincidence circuit; each coincidence would record the lifetime of a positron, measured by the delay that is introduced. More advanced methods are now used, and typical results are shown in figure 2.

Positronium formation and reactions in gases

Quenching of *o*-Ps—the most readily observed result of reactions—occurs by two distinct processes. One, conversion quenching, results from a collision with a molecule, changing the *o*-Ps to *p*-Ps and thereby increasing the annihilation rate. The other, pick-off quenching, is the process by which the positron in positronium interacts with an electron in a molecule and annihilates with it, rather than with the electron with which it starts. It is the observation of anomalous rates in these quenching effects that has led to the suggestion that positronium compounds are formed. Thus there is in the rare gases no reason to suspect any other effect than pick-off quenching in interpreting the results of three of the experiments that have been tried [4, 5].

Equally, no chemical compounds having unpaired electron spins are involved in the conversion quenching that occurs readily in the presence of gases such as nitric oxide and nitrogen dioxide. In other gases, such as chlorine and bromine, the quenching effect of the gas on the *o*-Ps lifetime must be ascribed to positronium compound formation. If a compound represented by (e^+e^-) Cl is formed, then positronium remains in a place of high electron density, instead of wandering round from molecule to molecule, and the chances of a faster annihilation are much increased. Such compounds have been suggested since the early work of M. Deutsch and his group [6], but very little research has been done on them. Theoretical calculations have shown that they will be

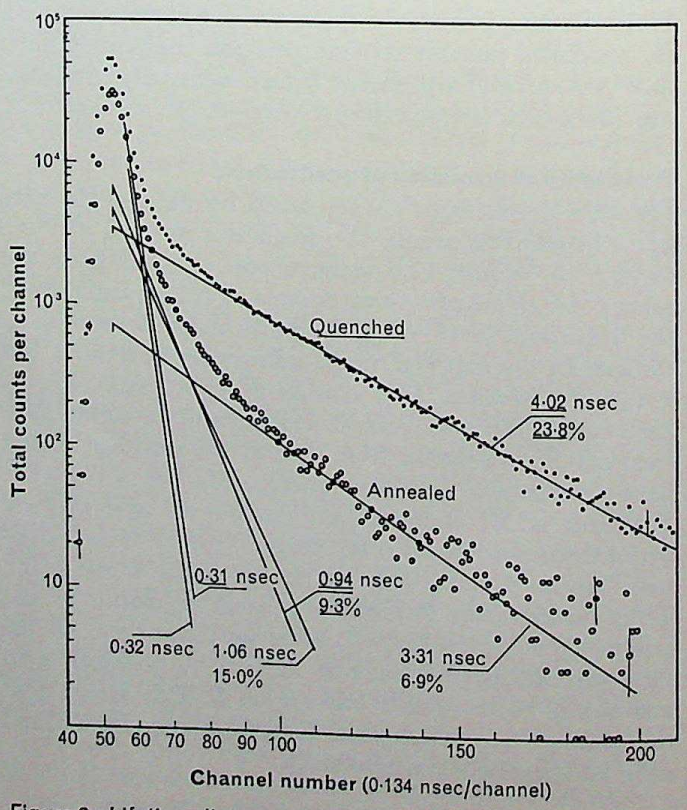

Figure 2 Lifetime diagram and component resolution for quenched and annealed polytetrafluoroethylene. [3]

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stable. For example, PsCl should have a bond energy of 1·55 eV, and an energy of formation of 34 kcal/mol. Some experimental evidence for this will be described later.

Some interesting results emerged in 1963 [7, 8]. These were interpreted to mean that compounds were formed between positrons which had failed to form positronium and various gases. In argon gas to which small amounts of methane, ethane, propane, n-butane, isobutane, or carbon tetrachloride had been added, the annihilation rates of positrons were found to be 3 to 700 times as fast as those predicted for free positrons by the Dirac formula

$$\lambda = n \times 0{\cdot}748 \times 10^{-14}\text{sec}^{-1}$$

where n is the number of electrons per cm^3 available for annihilation. It is almost certain that the positrons annihilate faster because they come near a much larger number of electrons that closely surround them in a molecule such as e^+CCl_4. In pure Freon-12, the lifetime of free positrons decreases as the pressure increases and it seems likely that the compound $e^+CCl_2F_2$ is formed. All of these compounds are stable, of course, only in the specialized sense that has already been defined.

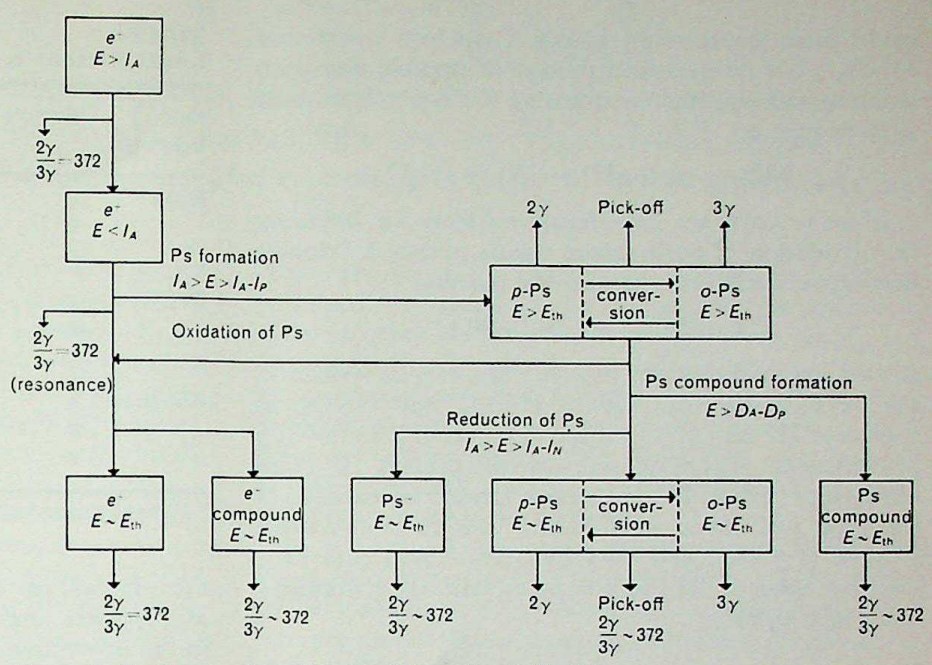

Figure 3 Positron and positronium interaction in liquids.
I_A = Ionization potential of substance A.
D_A = Dissociation energy of substance A.
D_P = Dissociation energy of positronium compound (e.g. bond strength of Ps-Cl).
E, E_{th} = Energy of positron and thermal energy (about 0·025 eV) respectively.
I_N = First ionization energy of Ps (0·20 eV).

Positronium formation and reactions in liquids

It is surprising, but understandable, that so much research was done on positrons in liquids and solids before much was really known about reactions in gases. The greater complexity of reactions in liquids is illustrated in figure 3, which represents present notions of the various fates of positrons and positronium [19].

In liquefied helium, it seems likely that, as D.A.L. Paul [9] suggested, the following reaction occurs with traces of oxygen:

$$Ps + O_2 \longrightarrow PsO_2$$

The radical PsO_2 is analogous to the well-known hydroperoxy radical HO_2. In quite pure helium there is some evidence pointing to the existence of a positron-helium compound [10].

In organic liquids, the researches of S. Berko [11], C. R. Hatcher [12], B. G. Hogg [13], and R. Stump [14] have explored the features of positronium formation and reactivity in a number of ways. For example, the results of Hatcher and Hogg for the halogenated benzenes and propanes are shown in Table III. This table shows two features: the electropositive nature of the halogen atoms decreases in the order F > Cl > Br > I and so does I_2, the proportion of the *o*-Ps component of the composite positron lifetime in the liquids. This suggests that the positron can approach the I atom and combine with the molecule, giving a smaller I_2, more readily than it can approach and overcome the Coulombic repulsion of the F atom. The table also shows that the attempt to apply the Ore model devised for gases to liquids is not helpful. The extension of the model to bromopropone and iodopropane provides no Ore gap at all, and this implies that no positronium should have been found in the experiments.

There is now a good deal of extremely interesting information on organic compounds. For example, a recent paper [15] suggests that the presence of dissolved oxygen in many organic liquids has a disturbing effect on the positronium lifetime. It is clear that it is now time to re-examine the mass of earlier results [16] and look more closely at this fascinating field.

R. E. Green and R. E. Bell [17], and de Benedetti and his group [18], initiated extensive studies of aqueous solutions. The former studied the conversion quenching of *o*-Ps by the lifetime method, and the latter used analysis by the 3γ-coincidence method. A large number of substances in aqueous solution, particularly paramagnetic ions and oxyanions, have been tested for their effect on the positron system. The paramagnetic ions naturally quench the *o*-Ps by conversion to *p*-Ps to varying extents. An interesting comparison can be made with the effects of the same ions on the quenching of the triplet state in liquid anthracene [20]. It was at first thought that nitrate ions captured positrons before they

Table III
Positronium formation in halogenated hydrocarbons

Compound	I (eV)	D (eV)	'Ore gap' D−(I−6·8) (eV)	I_2 (%)
C_6H_5F	9·19	4·98	2·5	24±2
C_6H_5Cl	9·07	3·72	1·4	14±2
C_6H_5Br	8·98	3·07	0·9	6±2
C_6H_5I	< 8·73	2·47	0·6	4±2
C_3H_7Cl	10·7	3·4–3·5	0·4	16±2
C_3H_7Br	10·29	2·9–3·0	−0·5	10±2
C_3H_7I	9·41	2·3–2·5	−0·1	4±2

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could form positronium giving a positron compound $e^+NO_3^-$, but de Benedetti thought it possible that positronium was oxidized by donating the electron in some such process as

$$NO_3^- + 3e^- + 4H^+ \longrightarrow NO + 2H_2O$$

More recently we have found evidence for believing that oxidation of positronium occurs mainly by double decomposition, in this case by the reaction

$$Ps + NO_3^- \longrightarrow PsO + NO_2^-$$

In fact, by analysing the positron lifetimes in systems of the oxyacids H_3PO_4, H_2SO_4, $HClO_4$, and HNO_3, as well as in HF and H_2O_2, it has been possible to develop a consistent argument for the assignment of bond strength to various Ps compounds formed in reactions of the type just given [23]. These are Ps-O (2·2 eV), Ps-OH (1·3 eV), Ps-I (2·5 eV), and Ps-Cl (2·0 eV). This last value should be compared with the theoretical value of 1·55 eV.

Positronium formation and reactions in solids

As might be expected, the thermalization time of positrons is very short in solids: for example, the time for gold has been estimated at about 10^{-10} sec. This makes the experimental study of positron interactions difficult, and it is only quite recently that equipment sufficiently sophisticated to measure such lifetimes precisely has become available. Measurements of angular correlation and other features of the annihilation radiation have always been capable of giving useful results [21]. Again, general studies of solids are not by any means as advanced as they are for gases and liquids. Such factors as trace impurities and adsorbed layers of oxygen have only recently been shown to influence positronium formation in solids, just as they do in liquids.

In metals, where the electrons are considered to move freely in the conduction band, it was for long thought that positronium formation was unlikely. However, lifetimes have been measured accurately [22], and further it seems that positronium formation in a free electron gas (and thus in a metal) is highly probable. This still leaves the study of positronium in metals and ionic crystals in a rather uncertain state, although recent studies of alkali halide crystals and alkaline earth oxides are providing useful evidence of positron bound states. In the outcome we may yet have another useful non-destructive probe for the study of these classes of solids.

In covalent (molecular) solids, the picture is now much clearer. It has always been known that positronium is formed but it is still difficult to identify any interactions causing quenching. The formation of positronium in solids such as anthracene, ice, and cyclohexane, and its alteration by melting or a crystal transition have made it clear that some correlation exists between positronium formation on the one hand, and crystallinity and density on the other. As an example, figure 2 shows the total and composite lifetimes of positrons in a solid polymer, polytetrafluoroethylene (PTFE or Teflon) before and after a heat treatment. 'Quenched' PTFE is about 40 per cent crystalline (that is, well oriented), the remainder 'amorphous'; the 'annealed' PTFE is about 70 per cent crystalline. If these results are analysed [23] it is found

Table IV
I_2 and I_3 fractions for positron annihilation in PTFE

Heat treatment	Sample*	I_2 (%)	I_3 (%)	I_2+I_3 (%)	$I_2/(I_2+I_3)$
None	a	11·4	17·5	28·9	0·40
	b	11·4	15·0	26·4	0·43
	c	11·4	15·9	27·4	0·42
Quenched	a	9·3	23·8	33·1	0·28
	b	9·3	21·2	30·5	0·31
	c	9·0	21·1	30·1	0·30
Annealed	a	15·0	6·9	21·9	0·68
	b	13·5	5·9	19·4	0·69
	c	15·4	11·2	26·6	0·58

* Different samples from the same sheet of polymer.

the *o*-Ps exhibits two lifetimes; the shorter is due to *o*-Ps annihilation after an enhanced 'resonance' interaction in the crystalline regions of the polymer, and the longer is due to a weaker interaction with the amorphous part of the polymer sample. Table IV shows some results of the ratios of the supposed crystalline *o*-Ps interactions to the total *o*-Ps in the polymer. These studies have been extended to cases where physical and chemical changes have been induced in the polymer by neutron-irradiation and gamma-irradiation. It is entirely possible that positronium may be very useful as a probe for polymer analysis and for the study of bio-polymers.

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Carboxylation in plants

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D. A. Walker

The main features of the photosynthetic cycle by which carbon dioxide is fixed have been known for some time, but they do not account fully for the experimental results. This article describes refinements of the theory and also discusses a number of 'dark' carboxylations.

Plants derive all of their carbon, and more than 90 per cent of their dry weight, from carbon dioxide in the atmosphere. As a million litres of air contains, on an average, only 300 litres of carbon dioxide, a plant must 'process' more than 6250 litres of air for every gram of carbon that it converts into carbohydrate, protein, or lipid. Normally, 99 per cent of the carbon dioxide that is extracted is fixed by photosynthetic reactions—carboxylations—during daylight. There are dark carboxylations, but these are normally so slow that they are outweighed by the losses incurred in respiration, and most plants lose a tenth or so of the daytime gains during the night. There are, however, some species in which dark carboxylation is so rapid that there may be a net uptake of carbon dioxide even at night.

The corresponding sequence of reactions in which carbon dioxide is fixed in photosynthesis was proposed by Calvin on the basis of work which was recognized by the award of a Nobel Prize in 1961. In this cycle (figure 1), carbon dioxide combines with the 5-carbon sugar, ribulose diphosphate, to give two molecules of phosphoglyceric acid. These are then reduced to trioses. This carboxylation and the subsequent reduction may be considered to occur three times for each turn of the cycle, so that three molecules of pentose and three molecules of carbon dioxide combine to give six molecules of triose. Five of these 3-carbon sugars then undergo a series of condensations and intramolecular transfers leading to the formation of three new molecules of ribulose diphosphate. The cycle is thus completed, the original carbon dioxide acceptor has been regenerated, and there is a net gain of one triose. The energy required to drive these reactions is supplied by the high-energy phosphate compound adenosine triphosphate (ATP) and the reduced form ($NADPH_2$) of nicotinamide adenine diphosphate (NADP), formerly called triphosphopyridine nucleotide (TPN). It is now known that the ATP and $NADPH_2$ are themselves replenished in light-driven reactions within the chloroplast, which thus constitutes an entire photosynthetic unit.

Many scientists have been inclined to believe that the establishment of this cycle left little of photosynthetic carbon fixation to be elucidated, but, as we shall see, its present form is certainly oversimplified. This article will deal with refinements which may be found necessary for a full understanding of light carboxylation, and with some of the dark carboxylations that are known to occur.

Photosynthetic carboxylation

The leaves of higher plants are ideally suited to the extraction of small quantities of carbon dioxide from large volumes of air. 'Growth movements' enable them to present the maximum surface area to the light, and stomatal pores (as many as 30 000 per cm^2) permit the necessarily massive gaseous exchange between the external atmosphere and the intercellular spaces. The actual sites of photosynthesis are the chloroplasts, and these sub-cellular bodies, like the leaves, can become orientated in such a way that they can absorb a large proportion of the incident light.

In one respect, the carboxylating system within the chloroplast seems to be the least efficient part of the whole machinery. It is now widely accepted that the primary carboxylation in photosynthesis is catalysed by ribulose diphosphate carboxylase. This enzyme is present in the chloroplast in large quantities, but when it is extracted, it requires relatively high concentrations of carbon dioxide (more than 6 per cent) to achieve its maximal velocity. This is rather surprising, because intact photosynthesizing organisms can fix atmospheric CO_2 in the light at very high rates (up to 180 μmoles per hour for each milligram of chlorophyll). Moreover, it is impossible that diffusion could maintain the carbon dioxide concentration at the enzyme surface at anything like the same level as it is in air (0·03 per cent), particularly in higher plants, where the stomata and the intercellular spaces must be penetrated before the CO_2 even enters into solution. Also, where the diffusion path is short (as it is in aquatic algae), photosynthesis runs at its maximum speed in a concentration of as little as 0·018 per cent CO_2. Although pre-incubation with Mg^{++} ions and ribulose diphosphate does enhance the enzyme's affinity for CO_2, the failure of the isolated catalyst to match the performance of the intact organism leaves some uncertainty about its precise role in photosynthesis, though it is possible that the enzyme could be altered by extraction, or even that its present characteristics might have persisted unchanged from a time when the level of

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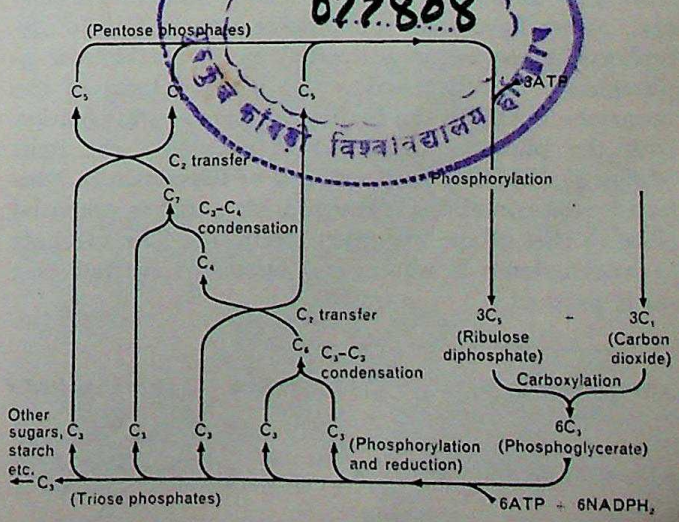

Figure 1 The Calvin cycle.

D. A. Walker, *B.Sc., Ph.D.*
Was born in Yorkshire in 1928 and was educated at King's College, Newcastle. He is now Reader in Enzymology in the Department of Botany, Imperial College, University of London.

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atmospheric CO_2 was much higher. The uncertainty also extends to the exact nature of the reaction which the enzyme catalyses. Even *in vitro*, the partial reactions are still unknown; however, it seems clear that, as Calvin proposed, one molecule of ribulose diphosphate yields two molecules of 3-phospho-glycerate (figure 2). The immediate energy source for this carboxylation is the substrate itself. It is assumed that this is to be carboxylated in the relatively unstable ene-diol form, since cyclic acetal formation is precluded by the smallness of the ring that would be involved.

In the living organism there is some evidence of a more reduced product, and it has been suggested that

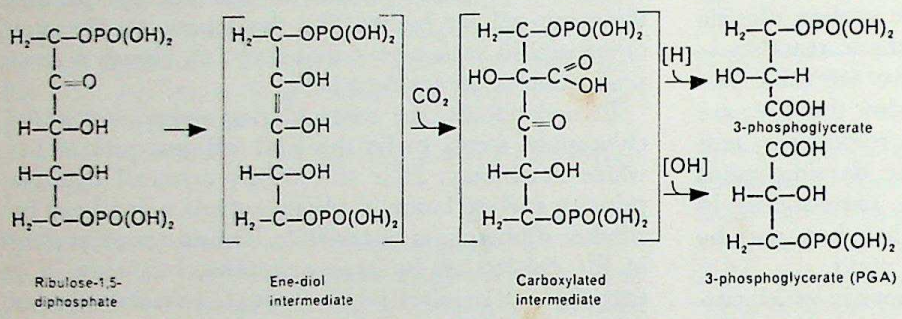

Figure 2

the carboxylated intermediate (figures 2 and 3) could be directly reduced so that, on hydrolysis, it would yield one molecule of phosphoglycerate and one molecule of glyceraldehyde-3-phosphate (figure 3) [1].

In photosynthesis, ribulose diphosphate is apparently rapidly replenished by the reactions of the Calvin cycle,

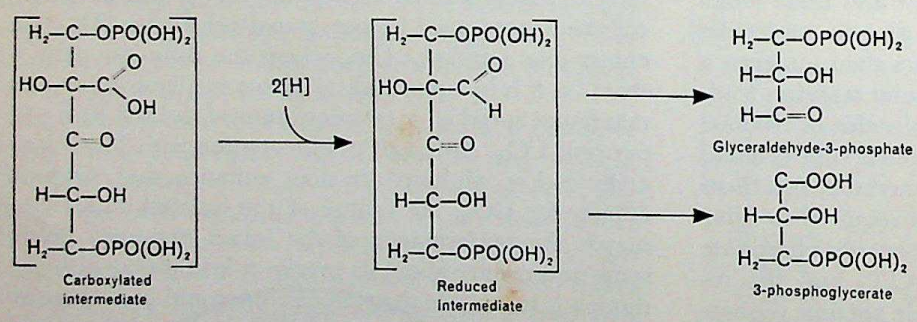

Figure 3

with ATP as the intermediary energy source. There is also, as we have said, a reductive step in which 1,3-diphosphoglycerate is converted to glyceraldehyde-3-phosphate; in this reaction the reduced form of the coenzyme NADP is the hydrogen donor. In association with the phosphorylation which occurs in the light (figure 4), NADP is itself reduced by ferredoxin (a non-haem iron-containing protein with a redox potential close to that of the hydrogen electrode). The ultimate hydrogen donor is water, and oxygen is evolved as a waste product.

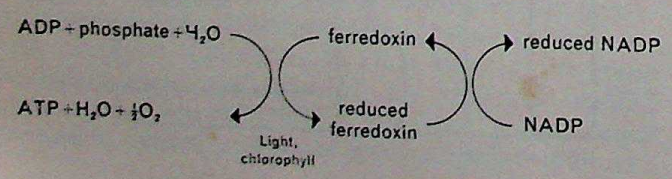

Figure 4

In the proposed reductive carboxylation of ribulose diphosphate (figure 3) ferredoxin might donate hydrogens directly to the carboxylated intermediate without the intervention of NADP.

Although most workers in the field consider the evidence for the main features of the Calvin scheme to be compelling, it is clear that modified environmental conditions can lead to substantially different photosynthetic products. Much of Calvin's work was done with relatively high concentrations of CO_2 (5 per cent), but when the carbon dioxide level is kept as low as it is in air, glycollate can become a major product. Its accumulation is also favoured by high light-intensities, by high oxygen-levels, and by the use of inhibitors such as isonicotinyl hydrazide and hydroxysulphonates. It is possible that glycollate is formed by a reaction in which a two-carbon fragment is split off from a sugar of the Calvin cycle (figure 5), but this and many other interesting features of glycollate metabolism have yet to be firmly established.

Isolated chloroplasts

One problem in the understanding of photosynthetic carboxylation now seems nearer solution. This is the reconstitution of a wholly adequate cell-free system. Chloroplasts which, when provided with a suitable hydrogen acceptor, would evolve oxygen at rates comparable with those of the intact plant were first isolated by R. Hill [3] in the late 1930s. This discovery gave the study of photosynthesis new impetus, and one of the many developments which was to follow in its train was the important demonstration by D. I. Arnon, M. B. Allen, and F. R. Whatley [4], in 1954, that isolated chloroplasts could themselves constitute a virtually entire photosynthesizing system. However, the rates of fixation were very low, and the situation

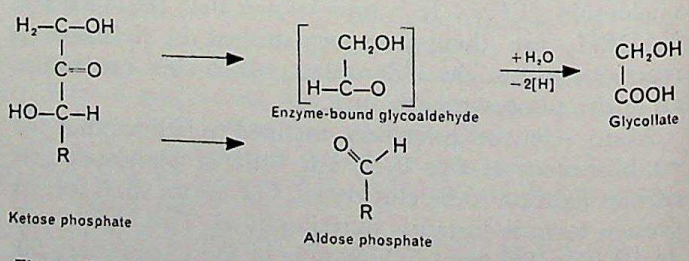

Figure 5

seemed to resemble that in the investigation of photosynthetic phosphorylation, in which the first reported rates were so small that their significance was questioned. For photophosphorylation such doubts were short-lived, because of the dramatic increases which followed, leading to the eventual achievement of rates which were more than sufficient to support photosynthesis in the intact leaf. The attempts to improve carbon dioxide fixation in isolated chloroplasts have not been rewarded by such large increases, and the best rates so far reported

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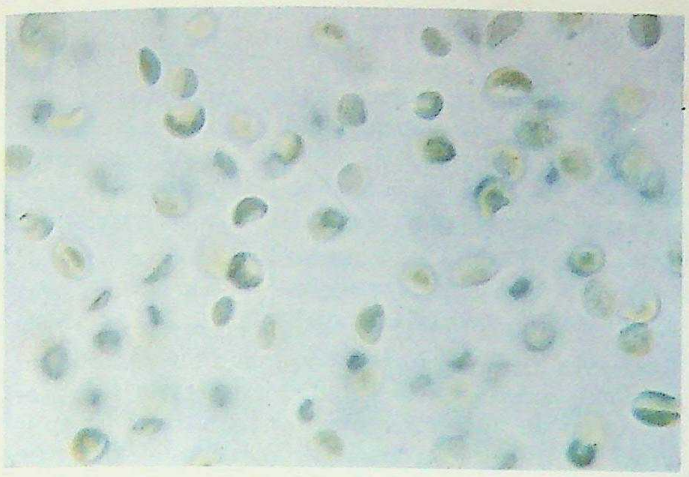

Figure 6 Whole chloroplasts (light microscope, ×350).

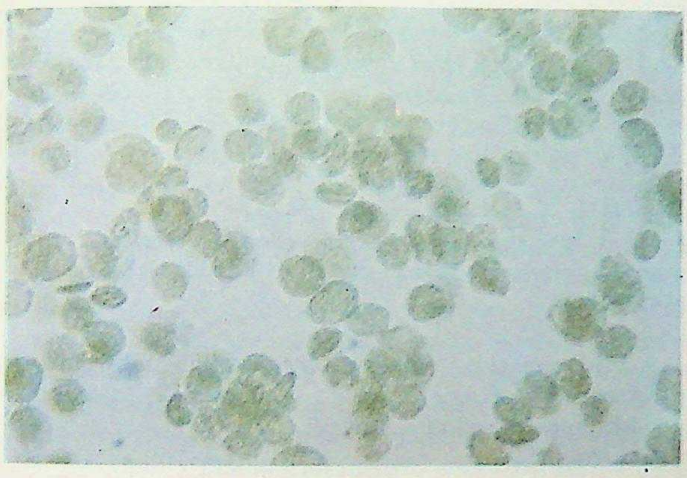

Figure 7 Membrane-free chloroplasts (light microscope, ×350).

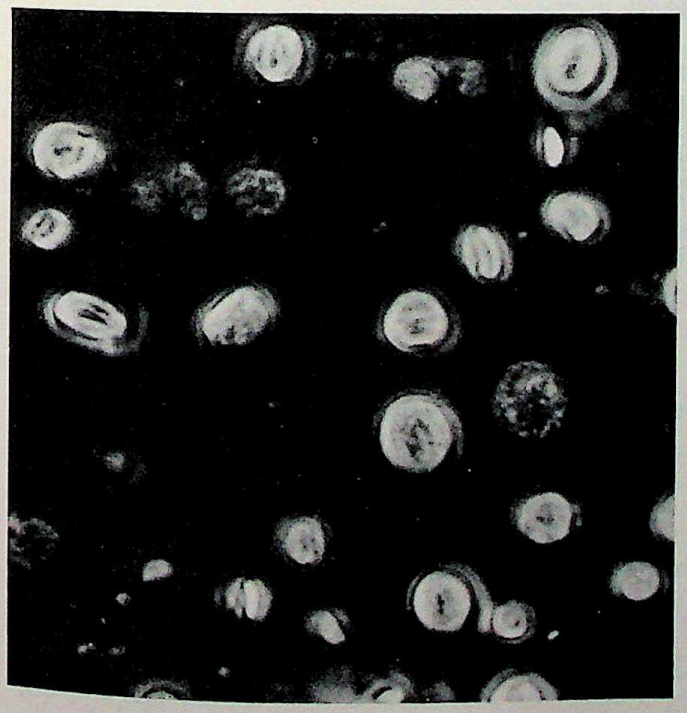

Figure 8 Chloroplasts under the phase-contrast microscope. Those that appear to have a halo are the ones with intact membranes. (×2000)

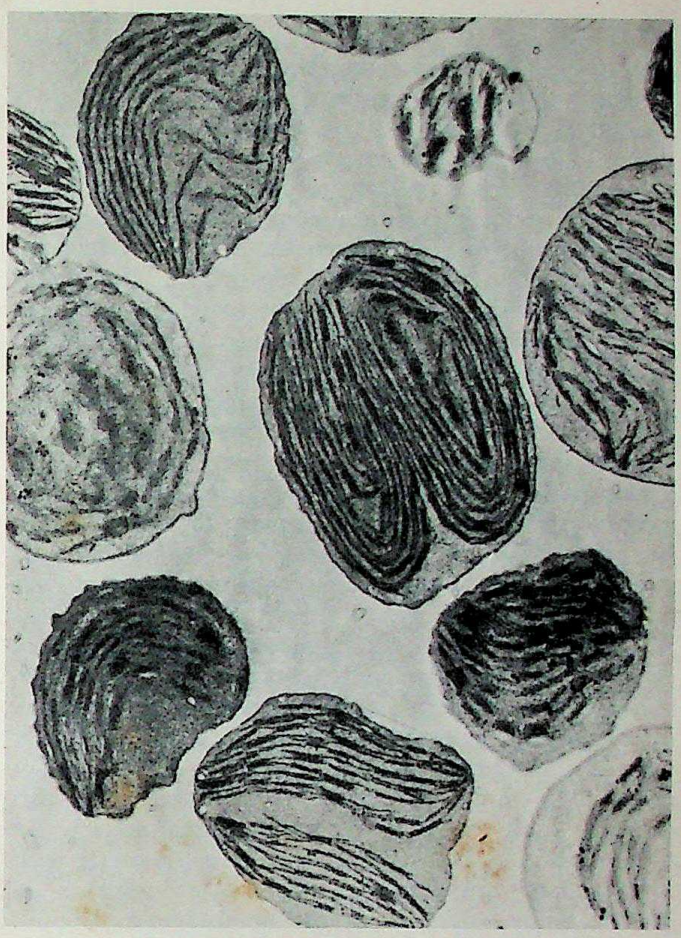

Figure 9 Whole chloroplasts (electron microscope, ×8000).

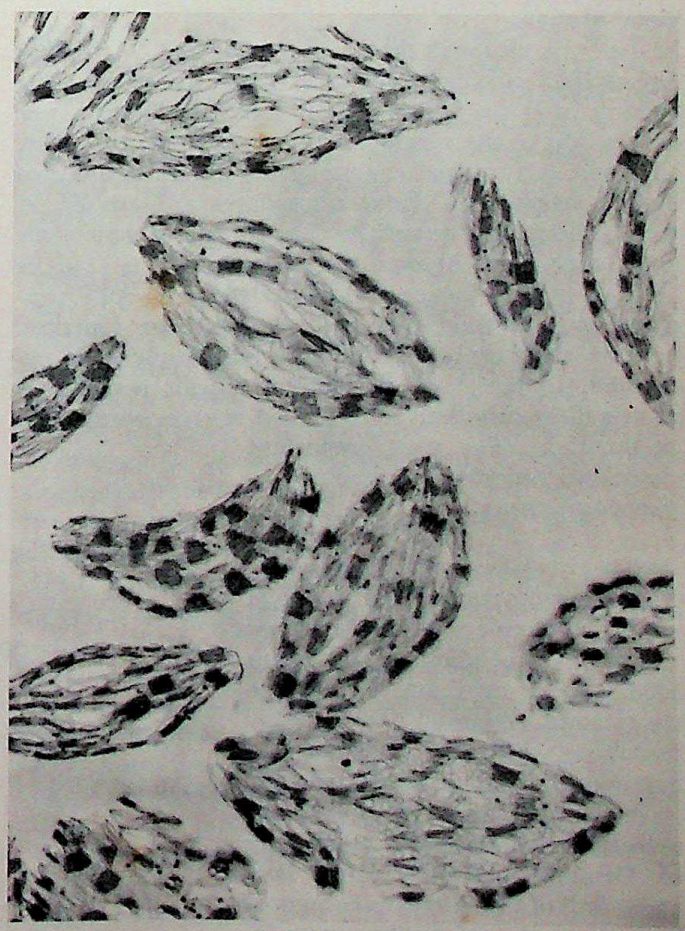

Figure 10 Membrane-free chloroplasts (electron microscope, ×7800).

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[5] are still only 10–15 per cent of those in intact tissues. The lowness of the rates has been attributed to loss of ribulose diphosphate carboxylase and of enzymes concerned in the regeneration of its substrate. Although there is no doubt that enzymes are lost from isolated chloroplasts, it is by no means certain that these losses are solely responsible for the poor rates. There are also surprising qualitative deficiencies in the products of carbon dioxide fixation by chloroplasts. Chromatographic analysis shows that in the most active chloroplasts, carboxylation, reduction, and phosphorylation are all proceeding at relatively fast rates: but it is a general experience that sucrose, a major end-product in intact leaves, is almost invariably absent.

Another problem, that has now been solved, is that of distinguishing whole and broken chloroplasts. Some preparative techniques yield chloroplasts that seem entire, but which have actually lost their membranes and their stroma (including presumably a large proportion of their enzymes). Work by W. O. James, R. M. Leech, and A. D. Greenwood [6, 7], involving a combination of gradient centrifugation and light and electron microscopy, has now established quite certainly that the grana in the isolated chloroplast become clearly visible only when the membrane is lost [8] (figures 6–10) and intact chloroplasts are specifically recognizable. By this criterion, chloroplast preparations which actively fix CO_2 contain a large proportion of chloroplasts with intact membranes. Suspending the chloroplasts in distilled water, which causes the membranes to rupture, leads to marked losses in activity.

'Dark' fixation

In the dark, although the reaction catalysed by ribulose diphosphate carboxylase can still occur, the rate of CO_2 fixation in green plants usually falls rapidly to 1 per cent or less of the maximum rate possible in the light, and there is a marked change in the nature of the products. Sucrose and sugar phosphates are formed in greatly diminished quantities, if at all, and organic acids and amino acids become the major products. This is because, in the absence of the $NADPH_2$ and ATP produced by light, the Calvin cycle can no longer function, because the supply of ribulose-1,5-diphosphate is exhausted. In the dark, the carbon dioxide acceptor is always ultimately derived from food reserves synthesized in the light. The most important single dark acceptor is probably phosphoenolpyruvate.

Reactions involving phosphoenolpyruvate

Phosphoenolpyruvate (PEP) is a 'high energy' molecule with a free energy of hydrolysis of about 13 kcal. This high value is attributable partly to electrostatic repulsion and opposing resonance within the molecule and partly to the intramolecular change, on hydrolysis, from the enol to the more stable keto form. In the presence of ADP and PEP transphosphorylase, about half of this energy is conserved in the formation of ATP, but the decrease in free energy is still such that the reaction is not freely reversible:

$$\text{PEP} + \text{ADP} \rightarrow \text{pyruvate} + \text{ATP} \qquad (\Delta F^b = -6{\cdot}3 \text{ kcal}) \quad \ldots(1)$$

(ΔF^b is the change in free energy calculated on the basis of conditions which could obtain in biological systems, for example, pH 7·0 and 0·01M reactants.) Alternatively, in the presence of PEP carboxylase, the available energy may be used to drive a carboxylation:

$$\text{PEP} + CO_2 + H_2O \rightarrow \text{oxaloacetate} + H_3PO_4 \qquad (\Delta F^b = -5{\cdot}7 \text{ kcal}) \quad \ldots(2)$$

Again only about half the available energy is used; the decrease in free energy is still large; and the equilibrium position is accordingly well to the right. It has been proposed that the energy required for the carboxylation is made available in a concerted reaction of the type illustrated in figure 11, and there is some experimental evidence that supports this view [9].

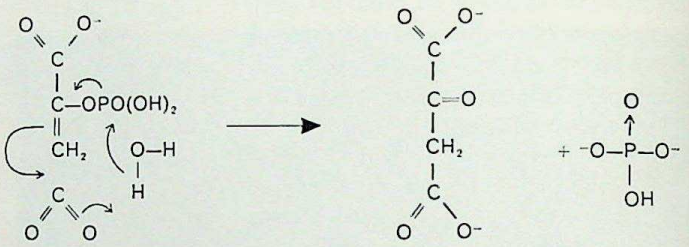

Figure 11 The simultaneous carboxylation and hydrolysis of phosphoenolpyruvate to yield oxaloacetate and inorganic phosphate.

A third reaction (catalysed by phosphoenolpyruvate carboxykinase) is one in which both carboxylation and phosphate transfer are achieved:

$$\text{PEP} + \text{ADP} + CO_2 \rightarrow \text{oxaloacetate} + \text{ATP} \qquad (\Delta F^b = 1{\cdot}28 \text{ kcal}) \quad \ldots(3)$$

Here all the available energy is utilized; the free energy change is actually slightly positive; and the reaction is freely reversible.

The role ascribed to these three reactions in intermediary metabolism (figure 12) is partly based on a consideration of these free energy changes [9–11]. Reaction (1), which has been known for many years, is the most likely link between the reactions of carbohydrate breakdown (which takes place in the cytoplasm) and the final oxidation of pyruvate to carbon dioxide and water in the Krebs cycle (which takes place in the

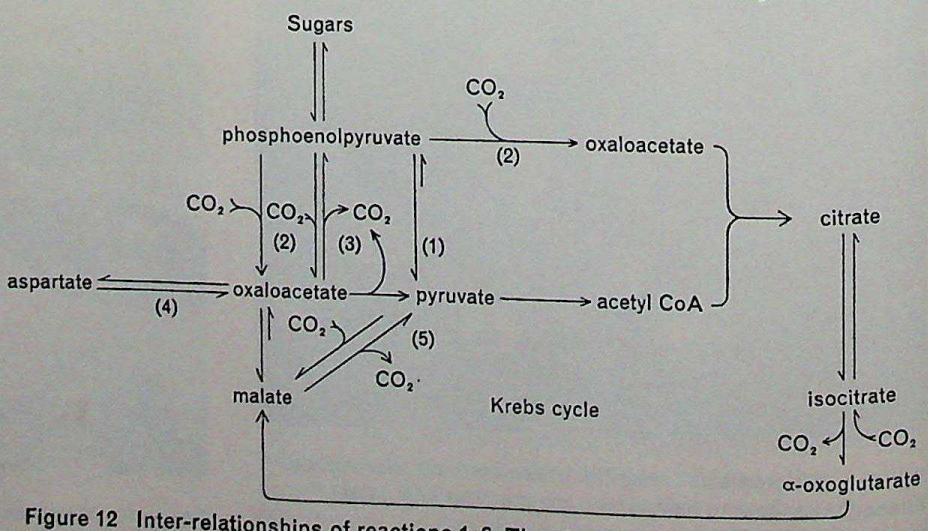

Figure 12 Inter-relationships of reactions 1–6. The size and direction of the arrows are intended to give some indication of the degree of reversibility.

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mitochondrion). Conversely, because of the high energy barrier, it is unlikely that the reverse reaction provides the main route of transfer from the Krebs cycle. Many plants need such a route. For example, in castor oil seeds, mobilization of lipid food reserves leads to a flow of acetyl coenzyme A into the cycle, and this is subsequently converted to sucrose before translocation to the developing embryo. The energy barrier in reaction (1) is very probably circumvented by reaction (3), which can thus provide a more easy route between the Krebs cycle and the reactions of carbohydrate synthesis.

Similar considerations implicate reaction (2) as the primary mechanism for the replenishment of cycle intermediates used in synthetic reactions. In growing leaves, for example, α-oxoglutarate will be converted to glutamate (for protein synthesis) and succinyl coenzyme A will be required for the formation of aminolevulinate in chlorophyll synthesis. Removal of these cycle intermediates cannot be made good solely by pyruvate which enters the cycle as acetyl coenzyme A, and therefore requires an acetate acceptor such as oxaloacetate. Reaction (2) can meet this requirement. Though usually thought of in the context of 'dark' fixation, this reaction catalysed by phosphoenolpyruvate carboxylase can occur equally well in the light, and indeed there is some evidence that it may account for between 3 per cent and 12 per cent of the carbon dioxide fixed. The affinity of the enzyme for CO_2 is much higher than that of ribulose diphosphate carboxylase, and the only important rate-limiting factor may be the extent to which phosphoglycerate is converted to phosphoenolpyruvate rather than to sugars. Even the lower value of 3 per cent would indicate that in many green tissues, where 'dark' fixation is less than 1 per cent of 'photosynthetic' fixation, more carbon dioxide may be fixed in this reaction by day than by night.

Crassulacean acid metabolism

In certain succulent plants, mostly members of the *Crassulaceae*, dark fixation occurs to such an extent that it leads to considerable acidification, and the leaves become detectably sour to the taste during the hours of darkness [12]. The oxaloacetic acid that is formed in reaction (2) is reduced to malic acid, which accumulates in the vacuole. In experiments with $^{14}CO_2$, aspartate also becomes heavily labelled, but there is no correspondingly large net increase in the level of this amino acid. It probably acquires much of its radioactivity by exchange transamination [11]:

$$\text{oxaloacetate-}^{14}\text{C} + \text{aspartate} \rightleftharpoons \text{aspartate-}^{14}\text{C} + \text{oxaloacetate} \quad \ldots(4)$$

Phosphoenolpyruvate carboxylase, which catalyses reaction (2), has a high affinity for CO_2 and is also inhibited by CO_2 in excess [11]. This is in accord with the known fixation behaviour of the intact plant. *Kalanchoë crenata*, for example, can remove virtually all the CO_2 from an enclosed space in the dark, and the levels of CO_2 which inhibit reaction (2) will also inhibit acidification in this species. The isolated enzyme introduces radioactive carbon specifically into the β-carboxyl of oxaloacetate or (in the presence of transaminase or malic dehydrogenase) into the corresponding carboxyls of aspartate or malate. In the intact plant, however, only two thirds of the radioactivity is present in this carboxyl (carbon-1), and the remainder is found in the other (carbon-4). This pattern of distribution is remarkably constant, and is independent of the duration of exposure to $^{14}CO_2$ or other variants in the experimental conditions. J. W. Bradbeer, S. L. Ranson, and M. L. Stiller [15] have explained this in terms of two carboxylations. The first, catalysed by ribulose diphosphate carboxylase, would yield two molecules of phosphoglycerate (one labelled and one not), and the second, catalysed by PEP carboxylase, would introduce label exclusively into the β-carboxyl of oxaloacetate, thus producing the '1/3 : 2/3' labelling pattern. The ribulose diphosphate required for the first sequence would be formed in the breakdown of carbohydrate and would not be regenerated in a cyclic fashion as in photosynthesis.

Although dark fixation almost certainly occurs in all plants, it attains considerable proportions in only a few [12]. As I have indicated, these are mostly succulents, and a question which immediately springs to mind is whether or not this massive dark fixation affords any ecological advantage. It may, because these plants often grow under arid conditions where their stomata, unlike those of most plants, open by night and close by day. Stomatal closure reduces water loss (an advantage in a dry environment), but it also interferes with the supply of CO_2 for photosynthesis. Dark fixation could theoretically replace at least some of the CO_2 shut out of the leaf by daytime stomatal closure. Indeed, G. Kunitake and P. Saltman [13] have shown experimentally that $^{14}CO_2$ incorporated into malate and related acids in the dark may be preferentially refixed into photosynthetic products during light deacidification. In theory, carbon dioxide conservation of this sort would not call for unreasonable energy expenditure. Assuming a double carboxylation [15] and the molecular rearrangements which are familiar features of pentose phosphate metabolism, eighteen molecules of carbon dioxide could be incorporated into twelve molecules of malate. This would require 12 molecules of reduced nicotinamide adenine dinucleotide (NADH) and six molecules of ATP (42 ATP equivalents in all). This is very close to the total energy (38 ATP equivalents) thought to be conserved by the cell in the complete oxidation of one molecule of glucose. If the energy bill were met from these sources, the net gain in CO_2 fixed would be a little less than 12 molecules for each molecule of glucose consumed. It should of course be borne in mind that, however much carbon dioxide from malate is actually refixed in photosynthesis, only three out of every eight carbons would have been initially incorporated by dark fixation. The remainder would be derived from carbohydrate and hence ultimately from photosynthesis. The fact that the atypical stomatal behaviour of succulents could itself be a consequence of massive dark fixation is interesting. Exposure to CO_2-free atmospheres can cause stomata to open in the dark in species in which they would normally close, and dark fixation can effectively remove all the CO_2 from the enclosed atmosphere. Conversely, high CO_2 concentrations can cause stomata to close in the light, and light deacidification (by producing CO_2) would therefore contribute to this end.

Oxidative decarboxylations

Although in most plants, the level of malic acid rarely approaches that in the *Crassulaceae*, it is frequently the

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most prominent acid in the vacuole. It is tempting therefore to suppose that malate might serve as an intermediary storage product, since it provides a link between the reactions of the Krebs cycle and those concerned in the initial stages of carbohydrate breakdown. Malate can enter the cycle unchanged, but it may also be decarboxylated in the reaction catalysed by Ochoa's 'malic' enzyme:

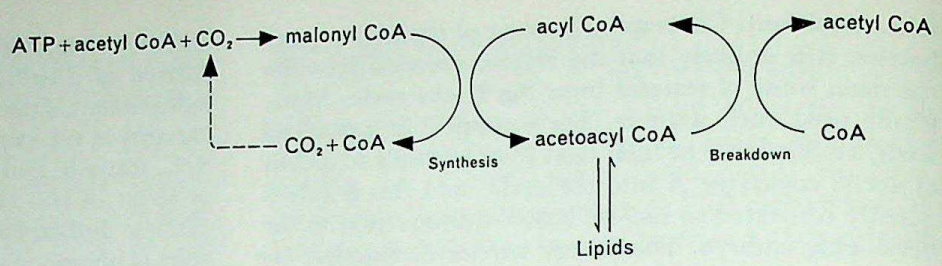

Figure 13

$$\text{Malate} + \text{NADP} \rightarrow \text{pyruvate} + \text{NADPH}_2 + \text{CO}_2 \quad (\Delta F^b = -0{\cdot}24 \text{ kcal}) \quad \ldots(5)$$

Although the equilibrium position favours decarboxylation, the reaction can be readily reversed by high concentrations of CO_2 and pyruvate. At a time when this reaction constituted one of the only two certain *in vitro* carboxylations, it was sometimes invoked, perhaps in desperation, as a means of fixation in everything from acid metabolism of *Crassulaceae* to photosynthesis. In fact, its characteristics make it generally unsuited to this role, and it seems more probable that it functions as a decarboxylating reaction, generating pyruvate and reduced NADP. In many respects it resembles two other oxidative decarboxylations. The first of these is catalysed by isocitric dehydrogenase:

$$\text{isocitrate} + \text{NADP} \rightarrow \alpha\text{-oxoglutarate} + \text{CO}_2 + \text{NADPH}_2 \quad \ldots(6)$$

and the second by phosphogluconate dehydrogenase:

$$\text{6-phosphogluconate} + \text{NADP} \rightarrow \text{ribulose-5-phosphate} + \text{CO}_2 + \text{NADPH}_2 \quad \ldots(7)$$

(All three reactions are also catalysed by enzymes which show a specific requirement for NADP and exhibit slightly different characteristics.) Freely reversible oxidative decarboxylations of this sort are often written as two partial reactions in which the oxidation precedes the decarboxylation. The best known example is, perhaps, the one which leads to the inclusion of oxalosuccinate in the Krebs cycle (as an intermediate in reaction 6). It is true that some of the enzymes concerned will catalyse some of the partial reactions postulated, but experiments with radioactive tracers provide no evidence to support the existence of free intermediates. The free-energy changes involved make concerted action, in which the oxidation and decarboxylation occur simultaneously [9, 11], more plausible. In the reverse reactions, the oxidation of reduced NADP could provide sufficient energy to drive the carboxylation, but the energy would have to be used before it is made available. Much the same considerations apply to reactions like the reductive amination of β-oxoglutarate, where the occurrence of a free imino intermediate seems most improbable.

Carboxylation in lipid synthesis

In an earlier paragraph I have discussed the possible role of carboxylation in circumventing the energy barrier between pyruvate and phosphoenolpyruvate. A similar system operates in lipid synthesis. When the work of F. Lynen and others led to the definition of the fatty acid 'spiral' (in which '2-carbon units' are split off from long-chain fatty acid derivatives as molecules of acetyl coenzyme A), it was at first supposed that lipid synthesis might be achieved by a direct reversal of these reactions. It is now clear, however, that the chain-lengthening molecule is malonyl coenzyme A [9]. This is formed from acetyl coenzyme A by an ATP-driven carboxylation. The free energy of decarboxylation then becomes available for the condensation [14] figure 13.

This is not entirely dissimilar to the metabolic sequence leading to the condensation of acetyl coenzyme A and oxaloacetate in the Krebs cycle, where the immediate energy input may be traced to the oxidative decarboxylation of pyruvate.

Conclusion

Plant carboxylation falls into two main divisions, photosynthetic and non-photosynthetic. It now seems reasonably certain that these are both essentially dark processes but that in the former the necessary reductants and high energy compounds arise as a direct consequence of photochemical events, whereas in the latter they are produced in respiration. Photosynthetic fixation is the primary source of carbon compounds in living organisms, non-photosynthetic fixation seems to be largely concerned with replenishing intermediates consumed in synthetic processes and in circumventing energy barriers in intermediary metabolism

Acknowledgment

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The design of strong materials

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A. H. Cottrell and A. Kelly

The ideal material for engineering purposes where strength is required needs to resist both plastic yielding and brittle cracking. Unfortunately, no one material can normally resist both modes of failure. This article describes how modern knowledge of the ways in which substances fail can be used to devise a very strong composite material in which fibrous components are embedded in a matrix.

The problem of designing from first principles a material suitable for the most arduous engineering work would seem to be a straightforward one. It should apparently be purely a matter of choosing a material according to the strength of the bonds holding its atoms together: this strength can be estimated from elastic or thermal properties, or calculated from atomic theory. The fact that coal then appears near the top of the list quickly dispels the illusion of simplicity. The strength of the atomic bonds gives us the 'ideal' strength of a material, but it tells us little about its real strength.

The actual achieving of real strength is made difficult by the fact that there are two different kinds of strength that a material may have—strength against plastic yielding, and strength against brittle fracture. Normally, a material can have only one of these, and not both. Thus soft clay yields easily, and so it is not brittle; if it is baked to harden it against yielding, it becomes brittle and breaks easily. The problem of building both kinds of strength into a material, despite their mutual exclusiveness, is a sophisticated exercise in applied science.

Ideal strength

The strongest solids are crystalline, because the regular arrangement and close-packing of the atoms allows the bonding forces to be deployed to best effect. There are two distinct ways in which a crystal can fail mechanically. Firstly, the atoms can separate by brittle fracture; this is similar to the breaking of glass, except that the fracture usually follows a particular cleavage plane in a crystal (figure 1b). Alternatively, the crystal may fail by shear, in which the atoms slide over each other on certain crystal planes along a crystal axis, producing plastic deformation (figure 1c).

Resistance to cleavage and to shear depends ultimately on the atomic forces. The strengths of everyday materials, however, are mostly limited by the presence of faults, and it has only recently become possible to make flawless materials and so realize in practice the ideal strengths promised by the theory of atomic forces.

The ideal cleavage strength, that is, the force required to break all the bonds acting through unit area of the cleavage plane, has been calculated exactly for a few crystals. A simple general way to estimate it is as follows. As the faces of the cleavage plane are pulled apart, the bonds are stretched against the tensile forces in them and they thus accumulate energy, since work is done during the stretching. The total work done on these bonds becomes the surface energy of the two cleaved faces, a quantity which can be measured by surface-tension methods. A relation can then be estimated between the ideal cleavage strength σ_t, the surface energy γ per unit area of the cleavage plane, and other known properties of the material. In this,

$$\sigma_t \simeq \sqrt{\left(\frac{E\gamma}{a}\right)} \qquad \ldots.(1)$$

where E is Young's modulus (the ratio of tensile stress to tensile strain at low strains) and a is the spacing between atoms.

The surface energy does not appear in the corresponding calculation of the ideal shear strength. The reason is that when the atoms slide along the shear plane, their bonds with neighbours across the plane are periodically renewed as successive neighbours are approached. No new surface is created, except for the steps at the ends of the plane; and because the bonds are repeatedly renewed, the process is less drastic than cleavage. The shear strength is therefore lower than the cleavage strength (table 1). The ideal shear strengths of soft materials such as copper, silver, and gold fall far below the ideal cleavage strengths, and the overall strength of such materials is clearly determined by plastic failure. For harder metals such as iron, and for non-metals such as diamond, sapphire (aluminium oxide), and magnesium

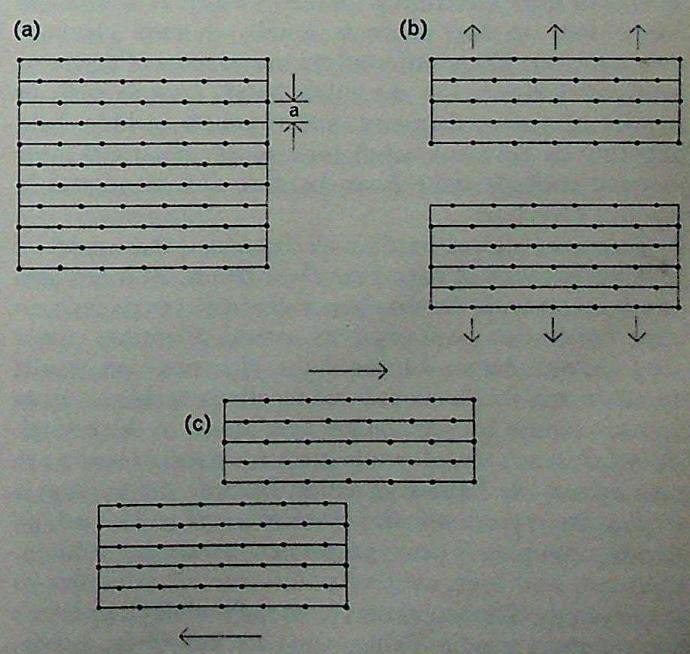

Figure 1 The perfect crystal shown in (a) can either be pulled apart in a direction normal to the atom planes as in (b) or else sheared into two pieces parallel to the atom planes as in (c).

A. H. Cottrell, *B.Sc., M.A., Ph.D., D.Sc., F.R.S.*
Was born in 1919, and was educated at the University of Birmingham. He was Goldsmiths' Professor of Metallurgy in the University of Cambridge from 1958 to 1965, and is now a Deputy Chief Scientific Adviser at the Ministry of Defence. His main scientific interest has been the development of an atomic theory of the deformation and fracture of solids.

A. Kelly, *B.Sc., Ph.D., F.Inst.P.*
Was born in 1929, and was educated at the Universities of Reading and Cambridge. His scientific interests are principally in the mechanical properties of solids.

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Table I
Ideal strengths of single crystals (1000 kg/mm²)

Substance	Ideal cleavage strength	Ideal shear strength
Copper	3·9	0·12
Silver	2·4	0·08
Gold	2·7	0·07
Iron	3·0	0·66
Diamond	20·5	12·10
Magnesium oxide	3·8	1·6
Sapphire	4·9	1·9

oxide, the shear strength increasingly approaches the cleavage strength. These shear strengths are of course expressed as the forces exerted tangentially on unit area of the shear plane. The shear plane generally lies at about 45° to the tensile axis, and so, when a crystal is pulled in tension, the resolution of forces on an inclined plane leads to an ideal tensile yield strength at least twice the ideal shear strength. The tensile strength expected of an ideal crystal must therefore be at least twice the value given in the third column of table I.

Atomic properties and ideal strength

The ideal cleavage strength is greater than the ideal shear strength, so that in many cases it is the ideal shear strength which sets a limit to the greatest strength that can be obtained in a perfect crystal. In seeking high ideal strength, we must therefore ask what determines the shear strength.

We see from figure 1(c) that, as the atoms slide over one another, the distances and the angles between neighbours across the shear plane both change. The relative importance of these two changes is very different in different types of crystals, and for this reason we cannot represent the ideal shear strength by one simple formula having an accuracy anything like that of equation 1.

Metal crystals shear easily because they are held together by free electrons, and not by covalent bonds. The energy of these electrons is markedly affected by changes of volume, so that there is usually a good cleavage strength; but it is unaffected by movements of atoms at constant volume. On the other hand, crystals such as sapphire, quartz, diamond, and titanium carbide, held together by covalent bonds (or strongly polarized ionic bonds), strongly resist shear, because such bonds act in specific directions.

To ensure high strength in all directions, there must be a dense network of strong covalent bonds. This requires small atoms with three or four valence electrons each, so that bonds can be formed in several directions about each atom. Atoms of the light elements are small; furthermore, the covalent bonding allows each such atom to have only a few immediate neighbours in the crystal. It is fortunate that crystals most resistant to shear are also among the lightest of solids. Because the binding is strong, the crystals are also elastically stiff and have high melting points. These properties—strength, stiffness, lightness, and high melting point—are all attractive to the engineer. The atoms that form such solids all lie in one part of the Periodic Table; they are beryllium, boron, carbon, nitrogen, oxygen, aluminium, and silicon. The very strongest solids generally contain one or other of these elements, and frequently no other element.

The observed breaking strengths of some of these very strong solids are shown in table II. For many engineering uses, the important properties are the ratio of strength to weight, and the value of Young's modulus per unit weight. Table II includes the values of these quantities for a very good modern structural steel, so that the potential superiority of the other materials can be seen. In practice, the very large breaking strengths reached in table II have usually been observed only in very small crystals, but there is no inherent reason why this should be so. Recently, large pieces of sapphire and boron have been made with very high strengths.

Table II
Observed breaking strengths of some strong materials (1000 kg/mm²)

Substance	Breaking strength	Young's modulus/Spec. gravity	Strength/ Spec. gravity
Sapphire	1·5	13	0·41
Carborundum	2·1	22	0·62
Beryllium oxide	0·7	12	0·21
Boron	0·7	17	0·28
Strong steel	0·21	2·6	0·03

Real strength

It is important in the design of strong materials to distinguish between brittleness, which is fracture with little or no plastic deformation, and fragility, which is fracture at very low stress with little deformation. What has to be avoided is of course fragility. The engineer, however, often considers fragility and brittleness as almost synonymous; this is because these two properties frequently go together in engineering materials. However, the clue to our later argument will lie precisely in stating that a brittle material is not necessarily fragile. The nature of the distinction is suggested by the fact that rubber is brittle but is certainly not fragile—it shows a large extension before failure.

Fragility will be avoided if the material can absorb a large amount of energy before it breaks. Energy, rather than force, is the important thing here, because the material has to withstand mechanical shocks in which only the energy is well defined: the internal forces involved will vary according to the way in which the energy is absorbed. The capacity to absorb mechanical energy without fracture is referred to as toughness; or, more exactly, as toughness when the energy is absorbed as plastic work, and as resilience when it is absorbed elastically.

These properties are closely related to the resistance of the material to the propagation of cracks. Figure 2(a) shows the formation of a cleavage crack of length $2c$ in a brittle material which is held at a constant tensile stress between fixed grips. The end of the crack must then appear as in figure 2(b), in which there are atomic bonds at every stage of elongation and failure. The maximum stress across the tip of the crack is therefore a true property of the material: it has the same value as the ideal cleavage strength σ_t, irrespective of the length and 'sharpness' of the crack. As the crack advances, the tip of the crack maintains its shape, and so each bond takes up the strain that previously 'belonged' to its predecessor. The cumulative effect of this over all the bonds is equivalent to the complete fracture of one bond as the crack

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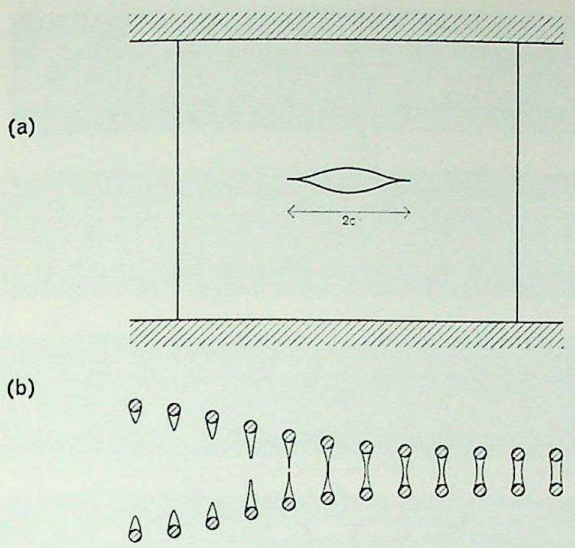

Figure 2 Formation of a cleavage crack.

advances by one atomic spacing, and the work necessary to do this is the surface energy as described above. Since the grips are fixed, this energy must come from the elastic strain energy of the body. It is intuitively obvious from figure 2(a) that a roughly circular region of radius c, about the centre of the crack, is released from stress and hence relieved of strain energy, by the presence of the crack. If the applied stress is σ, this energy is $(\pi c^2\sigma^2)/2E$ per unit thickness perpendicular to the diagram. Approximations are used in this calculation, and a more exact one gives just twice this value $(\pi c^2\sigma^2)/E$. The crack can grow if the rate of release of elastic energy is at least as large as the rate of increase of surface energy, that is, if

$$\frac{d}{dc}\left(4\gamma c-\frac{\pi c^2\sigma^2}{E}\right)=0 \qquad \ldots.(2)$$

where the factor 4 allows for the fact that there are two growing surfaces at each end. This gives the fracture strength as

$$\sigma \simeq \sqrt{\left(\frac{E\gamma}{c}\right)} \qquad \ldots.(3)$$

which is the famous formula of A. A. Griffith [3]. Equation 1 gives the ideal strength $\sigma_t=\sqrt{(E\gamma/a)}$. Since everyday objects contain cracks or similar flaws for which c (the radius of the circular region of the crack) is very much larger than a (the distance between atoms), the practical strength σ falls far below the ideal strength σ_t. This explains the fragility of most brittle materials.

Rubber is exceptional because its 'bonds' are randomly crumpled polymer chains, which can stretch enormously before they break. There is no reason to restrict the analysis used above to the case in which figure 2(b) represents the breaking of nearest-neighbour atomic bonds: the breaking of bonds shown there could equally well be the unravelling of polymer chains, the stretching of filaments of adhesive in a glued joint, or even, with certain geometrical restrictions, the stretching of a ductile metal by plastic deformation. The important point in all these examples is that the elongation needed to break the bond is enormously increased. Since 2γ on this interpretation is the work of fracture, that is, fracture-stress multiplied by elongation, γ in equation 3 is correspondingly increased to a value far above the true surface energy. The fracture strength is then much less reduced by the presence of the crack—the material is much tougher. The importance of this fracture toughness in engineering steels has been emphasized recently in an article in ENDEAVOUR by L. Rotherham [1].

Since the ideal shear strength is smaller than the ideal cleavage strength, how can a crack with the form of that shown in figure 2(b) ever appear in a crystal under stress? In the opinion of the authors, this is possible because the highly stressed bonds in the tip of the crack are surrounded on all sides by material at lower stresses, and are thereby geometrically constrained from relaxing plastically. In other words, a large part of the stress state in the critical region is hydrostatic tensile stress, not shear stress. From the theory of notches, we might expect the maximum shear stress in this region to be about one-sixth of the tensile stress σ_t. On this basis, and using the values in table 1, we would expect brittle cleavage to be impossible in copper, silver, and gold; marginally possible in iron; and fully possible in the other materials listed. This broadly agrees with observation.

Strong metals and alloys

The ductile metals are protected against cleavage failure by their plastic softness, but this softness limits their mechanical strength. The ideal shear strength is rarely achieved in practice, except in specially grown 'whisker' crystals [2], because most crystalline materials contain dislocations. A dislocation is an irregularity in the structure of the crystal which enables plastic shear to occur more easily (figure 3); its action is very similar to that of the wrinkle that can be pushed along to slide a heavy carpet easily across a floor.

In most metals, dislocations move rapidly under applied shear stresses that are only a fraction of those in table 1. On the other hand, in many non-metals, such as diamond and sapphire, dislocations are immobile except at high temperatures, and the strength of these crystals at low temperatures is not reduced if dislocations are present. The main problem of physical metallurgy has thus been to raise the plastic yield strength of metals by building into the crystals various features that would obstruct the movement of dislocations. The alternative is to eliminate all dislocations from the crystals, but this is extremely expensive. It is also dangerous, because such a crystal, once it began to deform plastically so that dislocations were created in it, would lose its shear strength catastrophically.

There are two main ways of blocking the movement of the dislocations. The first uses work hardening. In this, the metal is rolled or hammered so that it is heavily deformed plastically, and this puts large numbers of dislocations into it. These dislocations mutually entangle one another's movement in various directions, with the result that none can move easily. The alternative method uses precipitation hardening, in which the dislocations are blocked by finely dispersed particles of a foreign substance. Each method may give yield strengths up to about one-third of the ideal shear strength in ductile metals.

Many outstanding engineering materials, such as strong steels and aluminium alloys, and strong nickel alloys for high temperatures, have been developed in these ways. But we can now understand the limitations of this approach. Firstly, it is unlikely that such strengths

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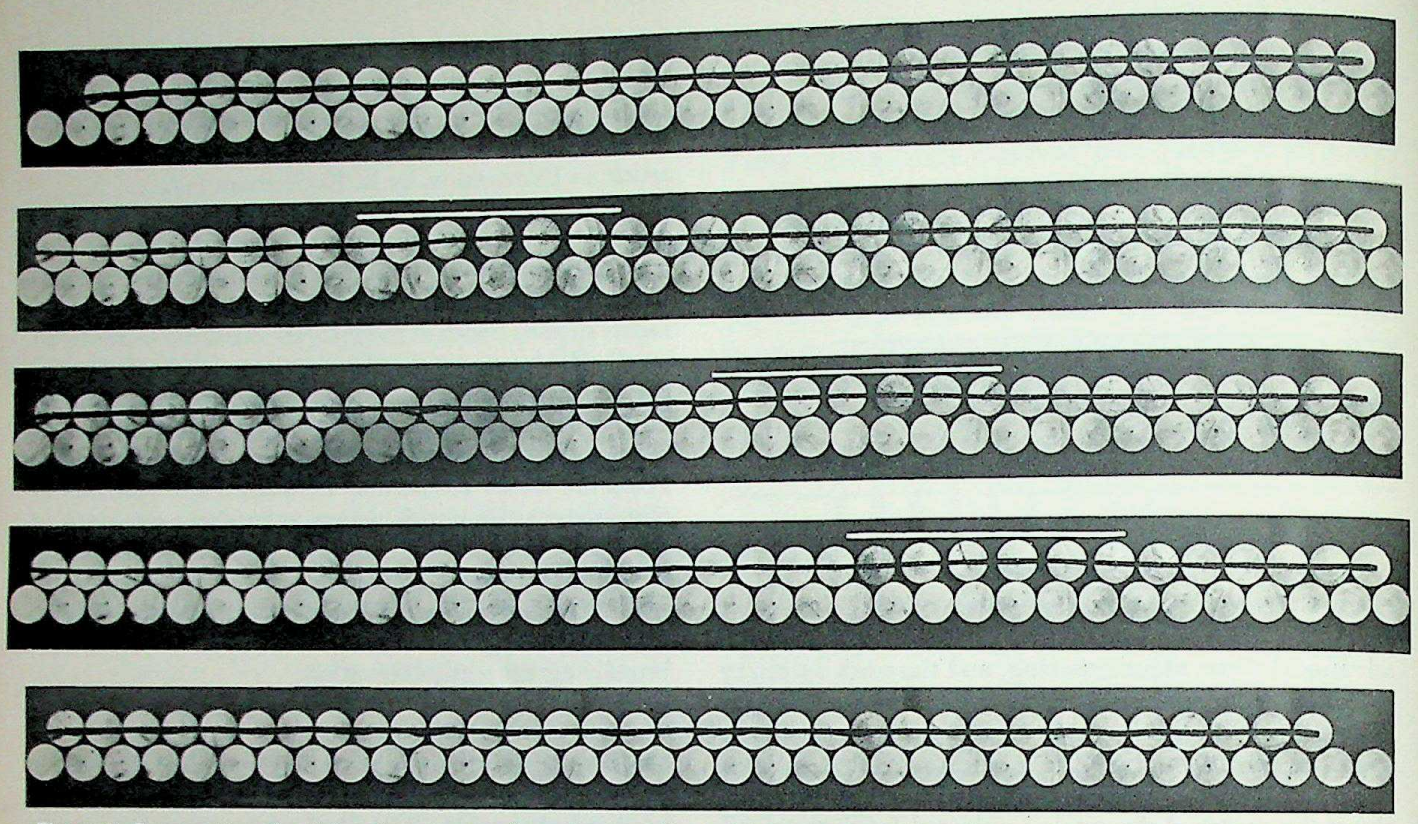

Figure 3 Propagation of a dislocation along a shear plane, as illustrated by wooden rollers. (By courtesy of E. N. da C. Andrade)

can be further increased more than about twofold; secondly, there is a great loss of strength at high temperatures, where the hard microstructures that give strength usually revert to soft ones; and thirdly, the methods do not take advantage of the superior ideal properties of the light covalent solids.

Tough brittle solids

To obtain real strength from the brittle covalent materials, we need some other method of stopping cracks, one that does not rely on plasticity. Nature gives us a simple clue to this. A bamboo stick is quite brittle, yet is not at all fragile. Even when sharply notched with a knife and then bent, it does not snap into two pieces. Splinters form near the notch, but no crack runs into the material, because it is impossible to sustain the penetrating crack structure of figure 2b across the weak interfaces between the fibres.

Paradoxically, then, we make the material strong by making it weak, that is, by laminating it with numerous weak interfaces that run parallel to the tensile axis. In place of the crack structure of figure 2(b) we shall then develop the structures of figure 4, which are harmless so long as they run along the tensile axis.

This principle opens the way to a solution of our problem. We must prepare the light covalent materials in the form of thin fibres, which have real strengths that closely approach their very high ideal strengths, and then join these fibres into parallel bundles, with a comparatively weak binding agent to provide the weak interfaces necessary for stopping cracks. Such a material, though brittle, is extremely strong even when sharply notched and hit with a hammer.

The structure and functioning of such a fibrous bundle are similar in some ways to those of a rope. In a conventional rope, the organic fibres, such as hemp, flax, or nylon, are themselves fibrous down to the molecular level, and for this reason are not individually sensitive to notches. Their strength is not lost if they rub together. Furthermore, they are very extensible and can be wound together. The load can thus be transmitted from one fibre to the next by sliding friction, and the helical arrangement of the fibres ensures that they grip more closely as they stretch and come together.

A bundle of strong stiff fibres, by contrast, requires a binding matrix for several reasons. The matrix will protect the surface of the fibres from scratches and chemical attack; it will cement the bundle into a composite solid with the necessary weak longitudinal interfaces; and it will transmit load from one fibre to the next. Resin is used in fibreglass laminates, but metals should provide excellent binders for stronger fibres, particularly for use at high temperatures. Unlike a resin, which is brittle, a metal can transfer load on to a fibre by plastic deformation. Consider a fibre rod embedded in a rod of metal with stress applied longitudinally, as in figure 5. The metal attempts to stretch plastically and so, because of its adhesion, tends to stretch the fibre elastically. A simple calculation shows that the stress σ thus developed in the fibre at a distance l from one end is given by

$$\sigma = \frac{4\tau l}{d} \qquad \ldots(4)$$

where τ is the tangential stress exerted on the surface of the fibre by the metal and d is the diameter of the fibre. This stress increases from both ends and so reaches the tensile strength σ_f of the fibre when the length of the latter exceeds a critical value l_c, given by

$$\frac{l_c}{d} = \frac{\sigma_f}{2\tau} \qquad \ldots(5)$$

This defines a critical ratio of length to diameter for the fibre to be broken by the plastic metallic binding material. Shorter fibres than this will not be used to their full

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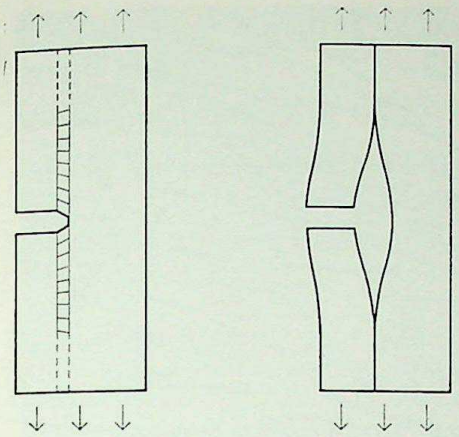

Figure 4 Obstruction of a crack by interfaces, weak in shear or tension, along the tensile axis.

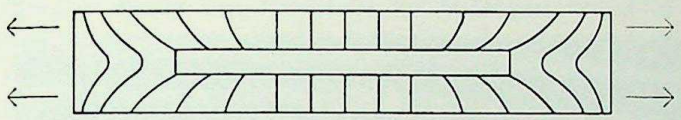

Figure 5 The stretching of a fibre rod embedded in a rod of metal.

capacity. In practice, it is necessary to use lengths of at least ten times l_c to obtain maximum strength. A parallel bundle of this type has an overall strength equal to σ_f multiplied by the fraction by volume of fibre in the material; this 'volume fraction' in a typical case would be 0·5. With very long fibres, it does not matter if τ is small. This means that the metallic binding material can be used almost to its melting point, and high strengths at very high temperatures are therefore possible.

The highest strengths are obtained when l_c is small and the fibres are very long. On the other hand, for greatest fracture toughness, l_c should be large and the fibres should be no longer than this. The strength is then lower, but the fibres tend to pull out of their sockets rather than break. There will be a large amount of mechanical work consumed in this, and the values of γ in equation 3 will be high for such materials. A large l_c can be obtained by using a metal with low yield strength or with a poorly adherent metal-fibre interface.

Manufacture

The manufacture of materials that are strong in more than one direction is complicated because, although the prescription for obtaining high strength by means of fibre reinforcement is a very simple one, it must be adhered to closely. High strength is obtained in the direction of the fibres. To obtain it in two directions, a laminated structure must be made, as illustrated in figure 6(a). It is no use preparing a mat of fibres as shown in figure 6(b): if this is done the strength will be lost.

To produce a fibre-strengthened body, long strong fibres must be made; they must be arranged parallel to one another; and they must be incorporated in a matrix that does not attack them chemically. The most straightforward method is to draw fibres of a glass and stick them together with a glue—this is the way that conventional fibreglass is made. Boron fibres can be produced in a form similar to that of silica glass, and these have been put in a resin matrix to make a material of great strength and with a much higher Young's modulus than that of fibreglass. Sapphire needles have been used in the same way, and a cheap material could be made with asbestos. The manufacture of materials for use at high temperature is complicated because there are no resins that are practicable above 200°C. However, silica fibres can be put into aluminium to provide a material for use at 400°C. The fibres are coated with aluminium as they are drawn and pressed together afterwards, so that the aluminium coatings bond to give a composite (figure 7).

Many of the strongest materials known today, such as graphite, silicon carbide, and beryllium oxide, are available in a strong form only as whiskers (figure 8). These whiskers are grown as a wool, which must be

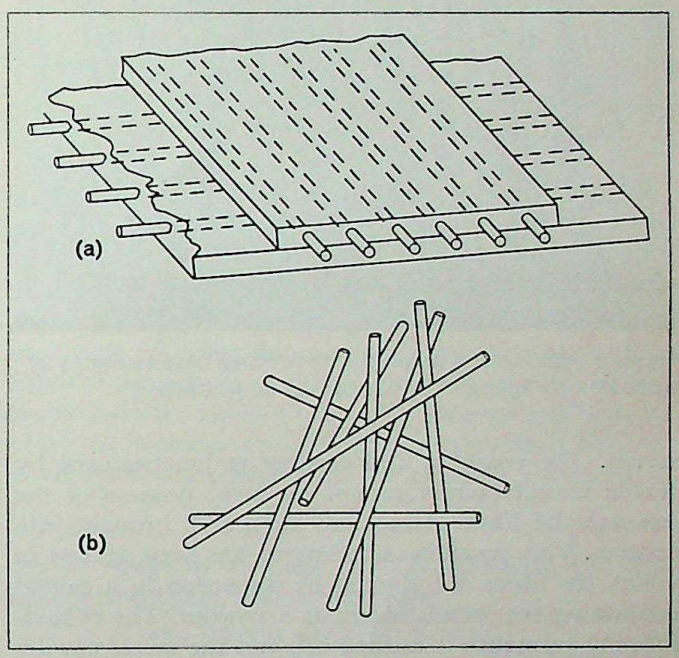

Figure 6 Possible arrangements of fibres. In (a) fibres are laid in parallel sheets and the fibres in successive sheets, are oriented at right angles. (b) An irregular arrangement of fibres prevents close packing.

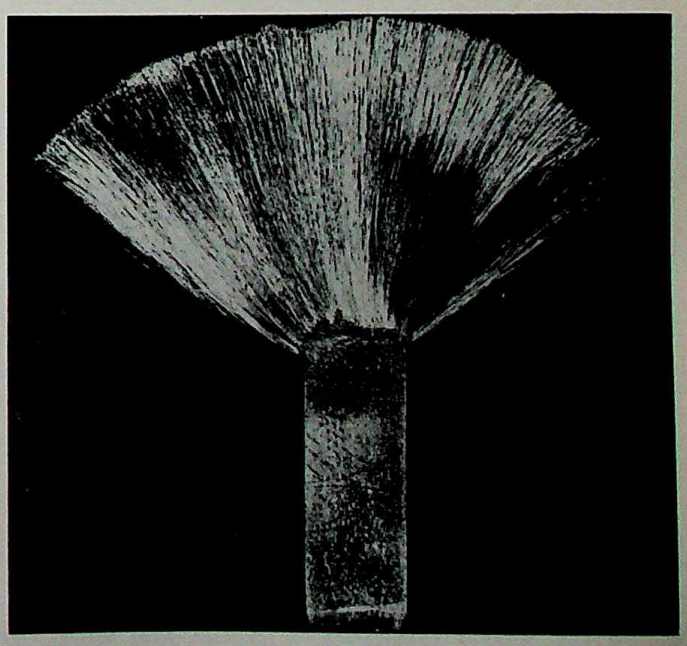

Figure 7 Silica fibres coated with aluminium can be pressed together to form a solid bar. (By courtesy of D. Cratchley)

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Figure 8 Whiskers of graphite. These fibres have strengths of up to $2{\cdot}1 \times 10^3$ kg/mm^2. (By courtesy of G. A. Cooper)

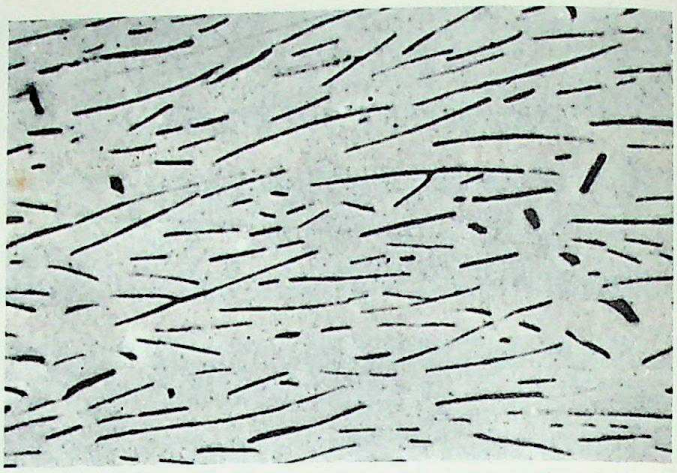

Figure 9 Flakes of graphite aligned in nickel. (By courtesy of R. P. M. Procter)

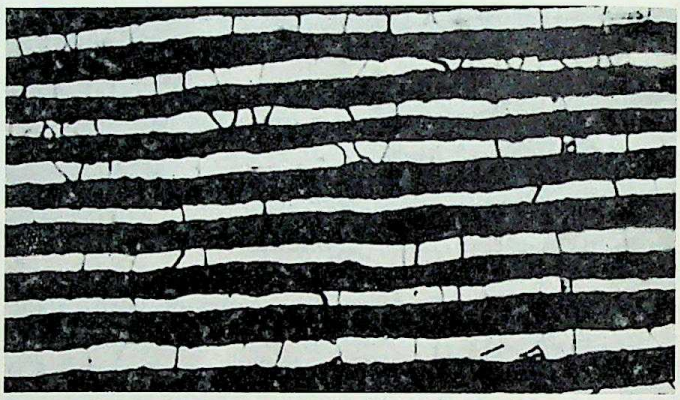

Figure 10 Bands of martensite (dark) in a ferrite containing aluminium. (By courtesy of R. L. Cairns)

sorted. The combing and carding techniques used by textile manufacturers cannot be used, because of the damage the fibres do to one another if brought into contact. Very recently, a technique has been devised in which the fibres are aligned by dispersion in a colloid containing the metal matrix as a powder. The colloid-forming substance is burned off, and the metal powder melted or sintered. Metals do not usually wet strong oxides, and the compacts made by melting the metal are therefore porous. Metals wet carbides, and with these, sound compacts can be made by melting the metal.

Crystals of some strong solids, such as graphite and titanium carbide, can be grown from a solution in molten metal. This of course suggests a method in which a large number of these crystals is grown in a fibrous shape and aligned in the required matrix. In principle, this could all be done in one operation that would be as simple as casting. It has not yet been achieved with very strong solids, but beautifully aligned microstructures have been made by the controlled solidification of some alloys. Thus figure 9 shows graphite flakes aligned in metal.

Fibrous microstructures in metal matrices can also be made by a process that operates entirely in the solid state. Figure 10 shows one produced by diffusion of aluminium into steel, so that alternate carbon-rich and carbon-poor regions are produced. Subsequent heat treatment of the steel by the standard metallurgical practice produces fibres of very strong martensite in soft ferrite.

Fibrous solids in engineering use

Present-day engineering practice, which has grown up round the special properties of metals and alloys, is about as suitable for strong fibrous materials as the horse carriage was for the internal combustion engine. Great changes will be needed if fibrous materials are to be used properly. The traditional methods of making things from metals—casting, forging, machining, riveting, and welding—will have to be replaced by methods of construction in which the finished body is completely made in one piece. In typical methods, the material is moulded on a former while the binder is still fluid, or a ribbon of the material is wound in criss-cross fashion on a former. Fibreglass boat hulls and pressure vessels are already made by these two methods.

Engineering design will also have to be transformed. The strength of these new materials is directional. Two-dimensional strength can easily be obtained by criss-crossing the fibres, but high strength along three axes is hardly possible, and engineering designs will have to take account of this fact. Because of their great strength, these materials will have to endure high elastic strains, and this will raise problems about the elastic stiffness of the structure. We can expect to see much more use of hollow structures made of thin strong membranes, interconnected and cross-braced for mechanical stability. Probably the greatest changes of all will come in architecture, because of the lightness of such structures. Perhaps the heavy masonry and square corners still used today will give way to a world of light airy domes and delicate tracery.

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Fluorocarbon derivatives of transition metals

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F. G. A. Stone

Organic compounds in which fluorine is substituted for hydrogen have been known for some time and are of considerable commercial importance. This article describes some of the ways in which these compounds can be made to form bonds with the transition metals, and the light that the resultant new compounds throw on the nature of the chemical bonds between carbon and metals.

A new class of chemical compound, in which fluorocarbon groups such as C_2F_5—, C_6F_5— or CF_2:CF— are bonded to transition metals, has recently been found [1]. These compounds bridge three well-established and long-known fields of study, which are concerned with organofluorine chemistry, with co-ordination chemistry, and with organometallic chemistry. It is widely known that fluorine atoms can substitute for hydrogen atoms in organic molecules, thereby modifying the properties of hydrocarbon groups and affording a range of fluorochemicals, some of which are important as refrigerants, polymers, anaesthetics, and aerosol propellants. Co-ordination chemistry and organometallic chemistry are perhaps somewhat less widely known. In co-ordination complexes, various groups, nowadays called ligands, donate an electron pair, or pairs, to a metal atom or ion, so as to fill some or all of the metal's vacant valence orbitals, and thereby stabilize a particular metal valence or oxidation state. Organometallic chemistry is concerned with the study of compounds in which one or more carbon atoms are linked directly to a metal atom. Probably the best known 'organometallic' is the technologically important compound tetraethyllead [$(C_2H_5)_4Pb$], now made in enormous quantities for addition to petrol as an anti-knock. (The estimated consumption for 1970 is 500 000 metric tons.)

Before describing some of the properties of the new fluorocarbon-metal compounds, some of the methods used to prepare them will be outlined. In order to appreciate their significance within the framework of chemistry as a whole, it is necessary also to survey briefly the ways in which chemists rationalize the bonding of organic groups to metals.

Synthesis

In the years immediately following the second world war, trifluoroiodomethane [CF_3I] and some of its homologues were prepared and studied at Cambridge [2]. These fluorocarbon iodides differed basically from their hydrocarbon analogues because of the strong electron-withdrawing power shown by CF_3 or similar groups. This 'electronegativity' is high, being about the same as that of a chlorine atom [3]. Consequently, the fluorocarbon iodides have properties which in some respects approximate more closely to those of an interhalogen like ICl than to those of an organic iodide. Now it had been known since 1928 that pentacarbonyliron [$Fe(CO)_5$] will react with iodine to afford tetracarbonyliron diiodide [$Fe(CO)_4I_2$], and in 1960 it was discovered [4] that the perfluoroalkyl iodides also react with this carbonyl. This means that the two reactions

$$I_2 + Fe(CO)_5 \rightarrow Fe(CO)_4I_2 + CO \uparrow$$
$$C_3F_7I + Fe(CO)_5 \rightarrow C_3F_7Fe(CO)_4I + CO \uparrow$$

are quite analogous.

The second of these reactions played a key role in initiating the study of the compounds we are concerned with in this article. The products, perfluoroalkyl(tetracarbonyl)iron iodides, were found to be stable in air in the crystalline state, which suggested that fluorocarbon groups in general could be bonded to transition metals to form stable metal complexes. In the last five years, several syntheses have been developed, the major reactions being summarized in figure 1. Many of these are applicable to other fluoro-organic compounds, and to different transition metals. Moreover, several of the compounds are already known to undergo reactions in which the fluorocarbon-metal group is preserved, leading to still more new compounds. For example, the complex

$$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OCH_3$$

can be made by treating $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ with sodium methoxide, and the complex

$$CH_3CF_2CF_2Mn(CO)_4P(C_6H_5)_3$$

is prepared by treating $CH_3CF_2CF_2Mn(CO)_5$ with triphenylphosphine. A substantial number of compounds in which various fluorocarbon groups are attached to transition metals have now been characterized.

Organometallic chemistry and the nature of carbon-metal bonds

The extent of organometallic chemistry is probably not generally appreciated. Nearly all metals are known to form compounds containing carbon-metal bonds. Those metals which are exceptions are almost certainly exceptions only because the metals themselves are very rare. E. Frankland prepared diethylzinc [$(C_2H_5)_2Zn$] in 1849, and the compound $KCl.PtCl_2.C_2H_4.H_2O$ was described by Zeise as early as 1827. Until comparatively recently (about 1951), research work was concerned principally with organo-derivatives of the metals of the main groups of the Periodic Classification, that is the metals in the groups Ia and IIa, and IIIb to Vb, of figure 3. Exceedingly little was known about the organic compounds of the transition metals, apart from the existence of a few metal-olefin complexes, such as Zeise's salt, which was shown some thirty years ago to contain the complex anion

$$[CH_2{:}CH_2PtCl_3]^-$$

Although there appeared to be some relationship between the olefin complexes and the metal carbonyls—tetracarbonylnickel or pentacarbonyliron, for example—

F. G. A. Stone, *M.A., Ph.D., Sc.D.*
Was born in Exeter, England in 1925, and educated at Cambridge. He worked at the University of Southern California from 1951 to 1953, and was an instructor and later an assistant professor at Harvard University from 1954 to 1962: he was a Reader in Inorganic Chemistry at Queen Mary College, London, from 1962 to 1963. Since then, he has been Professor of Inorganic Chemistry at the University of Bristol. His particular research interests are in the chemistry of organometallic compounds.

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Reaction between alkali metal salts of metal carbonyls and acyl halides:

$$2C_3F_7COCl + Na_2Fe(CO)_4 \xrightarrow{\text{tetrahydrofuran}} (C_3F_7)_2Fe(CO)_4 + 2NaCl + 2CO$$

$$C_6F_5COCl + NaMn(CO)_5 \xrightarrow{\text{tetrahydrofuran}} C_6F_5COMn(CO)_5 + NaCl \xrightarrow[\text{heat}]{} C_6F_5Mn(CO)_5 + CO$$

Reaction between fluorocarbon iodides and metal carbonyl complexes:

$$\pi\text{-}C_5H_5Co(CO)_2 + CF_3I \xrightarrow{\text{benzene}} \pi\text{-}C_5H_5Co(CO)(CF_3)I + CO$$

Addition of transition metal hydrides to unsaturated fluorocarbons:

$$HCo(CO)_4 + CF_2{:}CF_2 \xrightarrow{\text{pentane}} HCF_2CF_2Co(CO)_4$$

$$HRe(CO)_5 + CF_2{:}CCl_2 \xrightarrow{\text{pentane}} HCCl_2CF_2Re(CO)_5$$

$$HMn(CO)_5 + CF_3C{:}CCF_3 \xrightarrow{\text{pentane}} H(CF_3)C{:}C(CF_3)Mn(CO)_5$$

Addition of alkyl or aryl derivatives of the transition metals to fluoro-olefins:

$$CH_3Re(CO)_5 + CF_2{:}CF_2 \longrightarrow CH_3CF_2CF_2Re(CO)_5$$

$$C_6H_5Mn(CO)_5 + CF_2{:}CF_2 \xrightarrow[\text{pentane}]{\text{ultraviolet light}} C_6H_5CF_2CF_2Mn(CO)_5$$

Action of Grignard or organolithium reagents on complex halides of transition metals:

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + C_6F_5Li \xrightarrow{\text{ether}} (\pi\text{-}C_5H_5)_2Zr(C_6F_5)_2$$

$$\textit{trans}\text{-}[(C_2H_5)_3P]_2PtCl_2 + C_6F_5Li \xrightarrow{\text{ether}} \textit{trans}\text{-}[(C_2H_5)_3P]_2Pt(C_6F_5)Cl + \textit{cis}\text{-}[(C_2H_5)_3P]_2Pt(C_6F_5)_2$$

$$\textit{trans}\text{-}[(C_2H_5)_3P]_2NiCl_2 + CF_2{:}CFMgBr \xrightarrow{\text{tetrahydrofuran}} \textit{trans}\text{-}[(C_2H_5)_3P]_2Ni(CF{:}CF_2)Br + \textit{trans}\text{-}[(C_2H_5)_3P]_2Ni(CF{:}CF_2)_2$$

Reactions between alkali metal salts of metal carbonyls and fluoro-olefins:

$$CF_3CF{:}CF_2 + \pi\text{-}C_5H_5Fe(CO)_2Na \xrightarrow{\text{tetrahydrofuran}} CF_3CF{:}CFFe(CO)_2(\pi\text{-}C_5H_5) + NaF$$

$$\text{cyclo-}C_4F_6 + NaMn(CO)_5 \xrightarrow{\text{tetrahydrofuran}} \text{cyclo-}C_4F_5Mn(CO)_5 + NaF$$

$$CF_2{:}CFCl + NaRe(CO)_5 \xrightarrow{\text{tetrahydrofuran}} CF_2{:}CFRe(CO)_5 + NaCl$$

Figure 1 Synthesis of σ-bonded fluorocarbon derivatives of the transition metals.

there seemed to be little connection with the more conventional organometallics like tetraethyllead or ethylsodium. In fact, we now know that these various compounds differ only in the mode of bonding of carbon to the metals.

As is well known, the more electropositive metals have relatively low ionization potentials, and acquire stable electron configurations in their compounds by loss of electrons, thereby forming ionic substances. This process is energetically possible even with some hydrocarbon groups. Hence the representation of ethylsodium as $Na^+C_2H_5^-$ and potassium and scandium cyclopentadienides as $K^+C_5H_5^-$ and $Sc^{+3}(C_5H_5^-)_3$, respectively, is consistent with the properties of these compounds. For metals that are less electropositive, and have substantial numbers of valence electrons—for example, lead with four valence electrons—it is energetically more favourable to share electrons with carbon to form covalent compounds. Thus in tetraethyllead, each carbon-lead bond involves the sharing of an electron pair between the two atoms, and the bond is concentrated (localized) along the inter-nuclear axis. In the language of molecular orbitals this is called a σ-bond. Such bonds occur in many organo-derivatives of main group metals and of metals of the zinc group. However, the organo-derivatives of the light metals lithium, beryllium, magnesium, and aluminium sometimes show a special type of covalent bonding (electron deficient [5]), where bonding orbitals encompass more than two atomic centres. It will be appreciated that the division between ionic and covalent organometallic compounds is arbitrary, in the sense that the σ-bonds in the covalent compounds will have a degree of ionic character that depends upon the electronegativity difference between the metal in question and the particular organic group to which it is bonded. Indeed, the partial ionic character of the bonds serves to strengthen them by resonance [6].

Following the serendipitous discovery of ferrocene, bis(π-cyclopentadienyl)iron, in 1951 (figure 2) [7–9], several years of intense research activity established that the formation of covalent bonds to carbon was a characteristic feature of the first, second, and third transition-metal series. During this period, novel complexes such as those shown in figure 4 were discovered; in many of these, carbonyl or tertiary phosphine groups are bonded

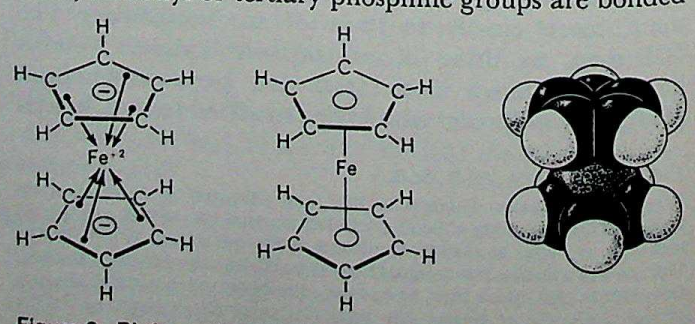

Figure 2 Bis(π-cyclopentadienyl)iron.

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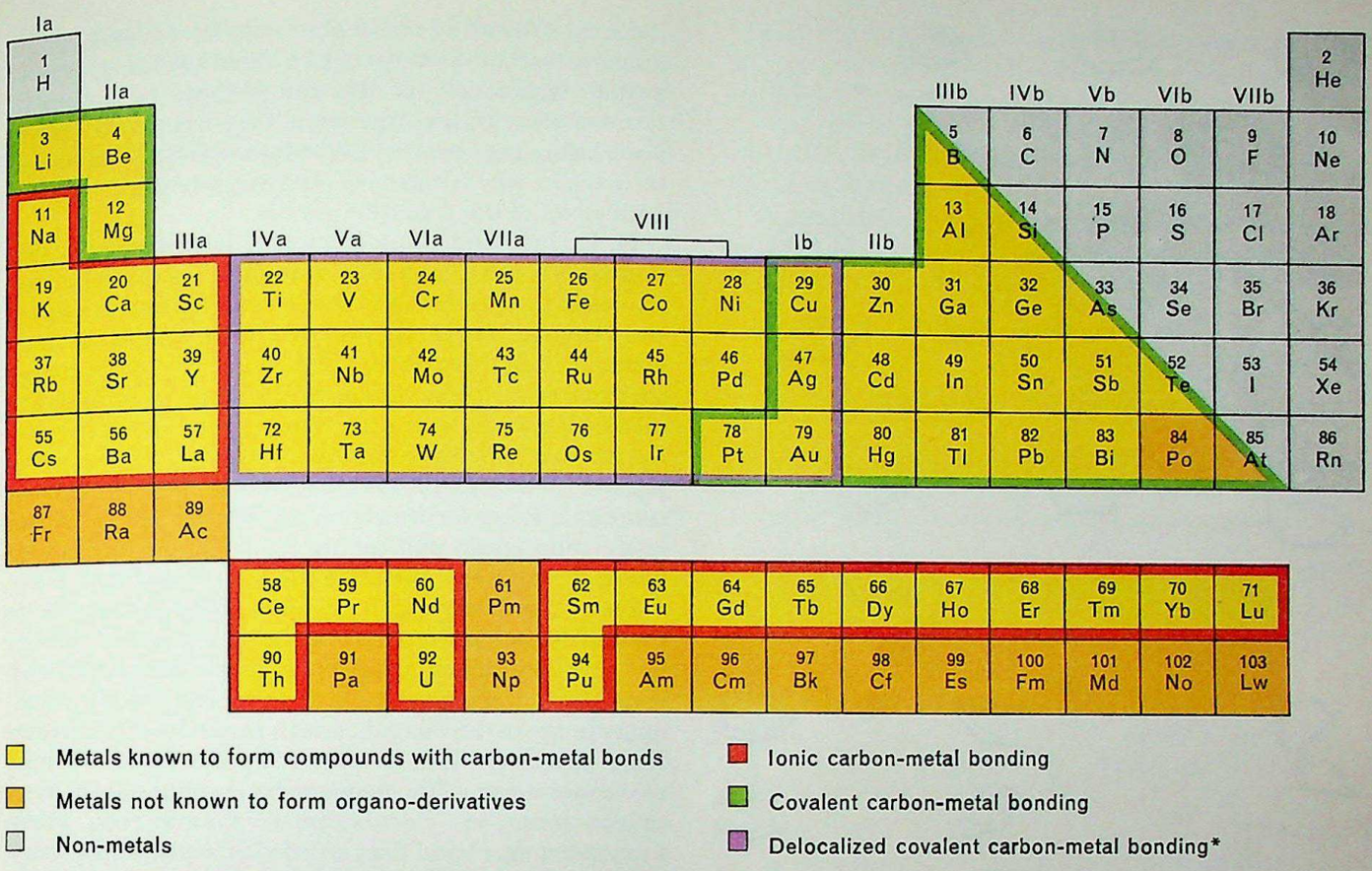

Figure 3 Periodic classification of organometallic compounds. The diagonal line through the metalloids separates the non-metals from the metals.

to the metals in addition to the unsaturated hydrocarbon groups [9]. The bonding of the hydrocarbon ligands to the metals involves their π-electrons. These electrons help to fill the bonding molecular orbitals of the resulting complexes in much the same way as electron pairs from the CO groups in metal carbonyls, such as tetracarbonylnickel (figure 5), fill the bonding orbitals in the carbonyls. It cannot be said that the nature of the carbon-metal bonding in all of these complexes is as yet completely understood, but it is generally believed that an important contribution to stability is the ability of the ligands (unsaturated hydrocarbon molecules, radicals or ions, carbonyl or phosphine groups) to accept electrons from the *d*-orbitals of the transition metals into various vacant ligand orbitals. This concept is pictorially represented in figure 5 for one of the CO groups in tetracarbonylnickel. It is a 'synergic' effect in which a classical donor bond from carbon to a metal is further strengthened by back donation of electron density from the metal to the ligand, resulting in the lowering of the energy of what would otherwise have been, in the absence of the effect, non-bonding *d*-electrons. The non-classical nature of the carbon-metal bonding, in that among other things it involves electron delocalization, must be emphasized. Moreover, in these complexes, the ligands provide many electrons for bonding so that all, or at least most, of the vacant low energy (bonding) molecular orbitals are filled. This state is known to favour stable complexes.

The classification of organometallic compounds in the above manner is a useful rationalization, but one should remember that differences in bond type are often a matter more of degree than of kind.

Properties of the fluorocarbon-metal compounds

In the last decade, several transition-metal complexes have been prepared in which alkyl or aryl groups are attached to the metals by apparently localized σ-bonds. One example is the methyl group in $CH_3Mn(CO)_5$. However, the outstanding feature of these complexes, indeed the factor that has permitted their successful synthesis, is that specific ligands are also attached to the metals. These ligands are of the kind mentioned above; they can supply the metal with sufficient electrons to fill bonding molecular orbitals. At the same time, by using their own vacant orbitals to accept electron density, they can lower the energy of the non-bonding *d*-electrons of the metal, thereby removing additional negative charge transferred to the metal atom by the σ-bonded alkyl or aryl groups. However, except for certain complexes of the nickel group metals, such as *cis*-$[(C_2H_5)_3P]_2Pt(CH_3)_2$ [10, 11], these transition-metal derivatives are not chemically robust. They tend to be sensitive to both air and moisture, and to be thermally unstable. The new fluorocarbon derivatives are considerably more robust. This is well illustrated by the thermal stability comparisons made in figure 6 between analogous compounds, and by the fact that the majority of the fluorocarbon derivatives have been stored, as crystals, in air for months, or in some cases even years, without decomposition. Moreover, several instances are known in which the fluorocarbon compound, for example $(C_2F_5)_2Fe(CO)_4$, exists, although the hydrocarbon analogue has never been synthesized. Thus transition metals have been 'conditioned' to form

* It should be realized that these bond-type classifications are not rigid. For example, titanium forms unstable $(CH_3)_4Ti$, and localized carbon-metal bonds can be stabilized by other ligands (see text).

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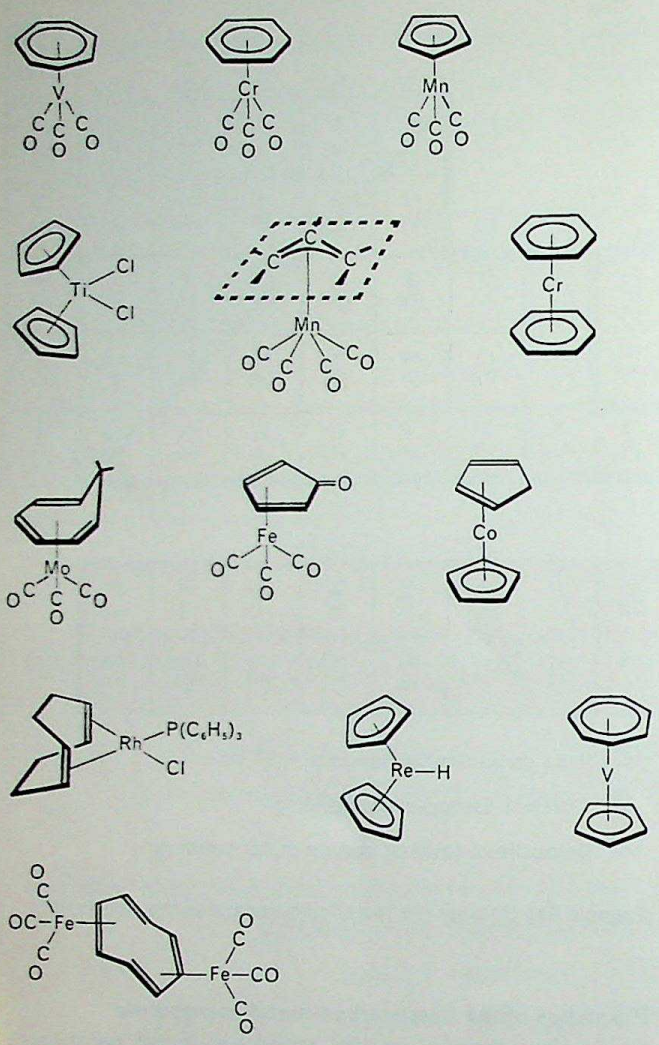

Figure 4 Some π-complexes of transition metals.

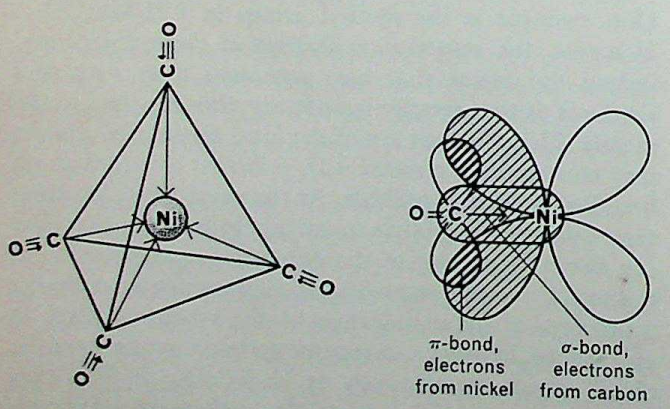

Figure 5 Tetracarbonylnickel.

$(C_2F_5)_2Fe(CO)_4$, dec. above 100°
$HCF_2CF_2Co(CO)_4$, stable at 25°
$CF_3Ni(CO)(\pi\text{-}C_5H_5)$, stable at 25°
$C_2F_5Mn(CO)_5$, stable up to 150°
$C_6F_5Mn(CO)_5$, stable up to 170°
$(C_6F_5)_2Zr(\pi\text{-}C_5H_5)_2$, dec. 218°
$HCF_2CF_2Mo(CO)_3(\pi\text{-}C_5H_5)$, dec. 100°
trans-$(C_6F_5)_2Ni[P(C_2H_5)_3]_2$, not dec. at 213°
cis-$(C_6F_5)_2Pt[P(C_2H_5)_3]_2$, not dec. at 160°

$(C_2H_5)_2Fe(CO)_4$*
$CH_3Co(CO)_4$, dec. −35°
$CH_3Ni(CO)(\pi\text{-}C_5H_5)$, dec. 0°
$C_2H_5Mn(CO)_5$, dec. 25°
$C_6H_5Mn(CO)_5$, dec. 100°
$(C_6H_5)_2Zr(\pi\text{-}C_5H_5)_2$*
$C_2H_5Mo(CO)_3(\pi\text{-}C_5H_5)$, dec. 80°
trans-$(C_6H_5)_2Ni[P(C_2H_5)_3]_2$, dec. 125°
cis-$(C_6H_5)_2Pt[P(C_2H_5)_3]_2$, dec. 151°
* Compound not known.

Figure 6 Some comparisons of thermal stability between fluorocarbon complexes and their hydrocarbon analogues.

localized σ-bonds of reasonable stability by making the attached carbon atom part of a fluorocarbon group. A partial explanation for this can perhaps be sought in terms of some of the arguments that were used several years before the discovery of the fluorocarbon compounds to explain the dearth of known σ-bonded organo-derivatives of the transition metals.

H. H. Jaffé and G. O. Doak [12] have suggested that normal σ-bonds from a carbon atom to a transition metal may well be weaker than those to main group metals for two reasons. Firstly, they have a lower degree of ionic character and therefore less of the ionic resonance energy that makes for stable bonds to the more electropositive metals of groups Ia and IIa. Apart from group IIIa and the lanthanides, the transition metals are less electropositive. Secondly, the covalent contribution to the bond stability is lower for transition metals than for the metals of the zinc group and for the main group metals that follow the transition metals in the Periodic Classification.

From the foregoing, it would appear reasonable to assume that an important factor in the enhanced stability of the fluorocarbon-metal compounds compared with their alkyl or aryl analogues, is an increase in the resonance energy of the σ-bonds, which results from the greater ionic character. This is caused by the relatively high electronegativity of the fluorocarbon groups. Or, in more refined terms, an electronegative fluorocarbon group forms a stronger bond than an alkyl or aryl group because it can cause the metal bonding orbital to contract more effectively, thereby making it less diffuse and increasing the overlap with the carbon orbital. A further consequence of the electron-attracting power of fluorocarbon groups would be that the electron pair forming the σ-bond with the metal would be more closely associated with the organic group than in the analogous alkyl or aryl compounds. Hence there would be less negative charge placed on the metal. This lowering of negative charge on a metal is a condition believed to raise the stability of metal complexes [13].

It seems reasonable that there should be inherent differences in character of the σ-bonds formed between metals and fluorocarbon groups on the one hand, and between metals and alkyl or aryl groups on the other. However, the novel properties of the fluorocarbon derivatives suggest that an additional factor may be important. According to molecular orbital theory, combination of a metal valence-orbital with a carbon valence-orbital produces a low energy (bonding) σ-orbital and a higher energy (anti-bonding) σ*-orbital. The electron pair fills the molecular orbital, and under normal conditions, for example, when hydrocarbon groups are involved, the σ*-orbital remains vacant, being too high in energy to take part in bonding with metal *d*-electrons. This may not be the case, however, when the carbon atom is part of a highly fluorinated group. The fluorine atoms would lower the energy of the σ*-orbital, perhaps enough to permit effective back donation of *d*-electrons from the metal to carbon [14]. If this occurred, it would tend to stabilize the carbon-metal bond further, because of removal of charge from the metal.

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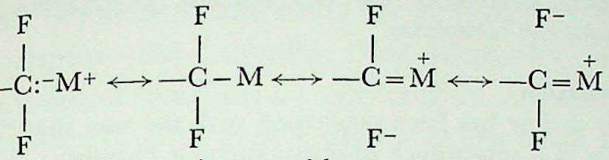
In classical terms, the electron-acceptor capacity of fluorocarbon groups, coupled with the introduction of additional ionic character into the σ-bonds already referred to, would imply resonance stabilization not possible with alkyl or aryl derivatives:



(M = metal atom with attendant ligands)

The relative contribution to the overall stability of the inductive (σ) and mesomeric ($d-\sigma^*$) processes is difficult to estimate, but there is chemical, spectroscopic, and X-ray crystallographic evidence that the fluorocarbon groups behave in the manner suggested. Several of the polyfluoroalkyl complexes of the transition metals are decomposed by aqueous bases to afford solutions containing fluoride ions [1]. This must mean that some of the C—F bonds in the fluoro-organic side chains are broken before the carbon-metal bonds. For a polyfluoroalkyl group, the hydrolysis of C—F bonds in this way is a most unusual and interesting property, but it is in accord with the idea of negative charge being removed from the metal and distributed over the fluorine atoms. Infra-red spectroscopic studies [15] on pentacarbonyl fluoroalkyl-manganese and pentacarbonyl fluoroalkyl-rhenium complexes in the carbonyl stretching region have enabled carbonyl-stretching frequencies to be measured, and force constants to be calculated. Moreover, the absorptions due to the C—F bonds occur at relatively low frequencies [16]. These results support the ideas concerning removal of charge from the metals, both by an inductive and by a mesomeric mechanism, that are expressed above. More definite evidence for these effects appears to be coming from X-ray structural studies made by R. Mason and D. R. Russell [17], and by M. R. Churchill [18]. Although only a few σ-bonded fluorocarbon-transition metal complexes have as yet been examined by X-ray crystallography, it appears that in those studied the carbon-metal distances are shorter than those in metal-alkyl compounds with normal σ-bonds.

Although the fluorocarbon-metal compounds are thermally more stable than their hydrocarbon analogues, they decompose if they are heated sufficiently strongly. The temperature at which decomposition occurs at an appreciable rate depends upon the nature of the fluorocarbon group and on the metal and other ligands. These thermal decompositions have usually been studied *in vacuo*, and a characteristic feature is the migration of fluorine atoms from the organic group to the metal with formation of some unsaturated fluorocarbons. Thus after 16 hours at 100°, the complex $(C_2F_5)_2Fe(CO)_4$ is very largely decomposed, forming a mixture of the fluoro-olefins $CF_3CF{:}CFCF_2$ and $CF_3CF_2CF{:}CF_2$, together with carbon monoxide. Occasionally this type of reaction has been used to obtain a new complex. For example, pyrolysis of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ at 150° affords small quantities of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$. This was the first method used to obtain this particular titanium fluoride.

Interestingly, chlorofluoro-organo-metal compounds are less stable and decompose with migration of a chlorine, rather than a fluorine, atom.

$$CH_3CF_2CFClMn(CO)_5 \xrightarrow{70^\circ} Mn(CO)_5Cl + CH_3CF{:}CFH\,^{1}$$

$$HCFClCF_2Mn(CO)_5 \xrightarrow{80^\circ} Mn(CO)_5Cl + CF_2{:}CFH$$

As with the fully fluorinated complexes, chlorine atoms in either α or β positions relative to the metal atom can migrate. Thus, on standing, a pentane solution of either

[1] The mechanism of formation of this fluorocarbon is obscure. It presumably arises from the radical $CH_3CF_2CF\cdot$.

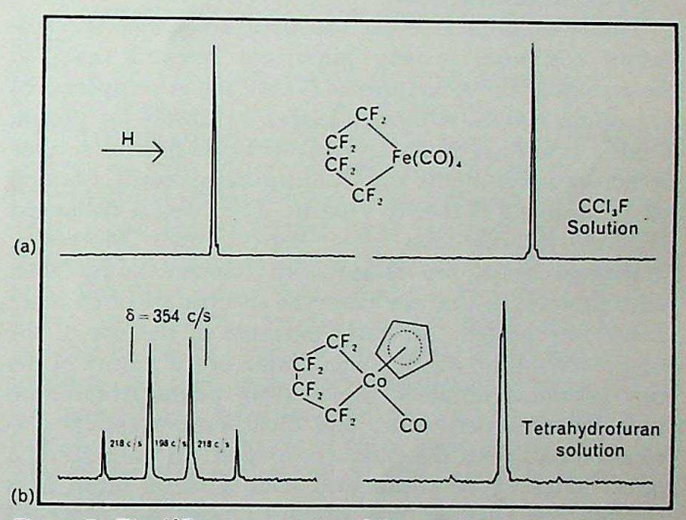


Figure 7 The ^{19}F n.m.r. spectra of the product of heating (a) pentacarbonyliron with tetrafluoroethylene and (b) dicarbonyl-π-cyclopentadienylcobalt with tetrafluoroethylene. The structures of the products are shown with the spectra.

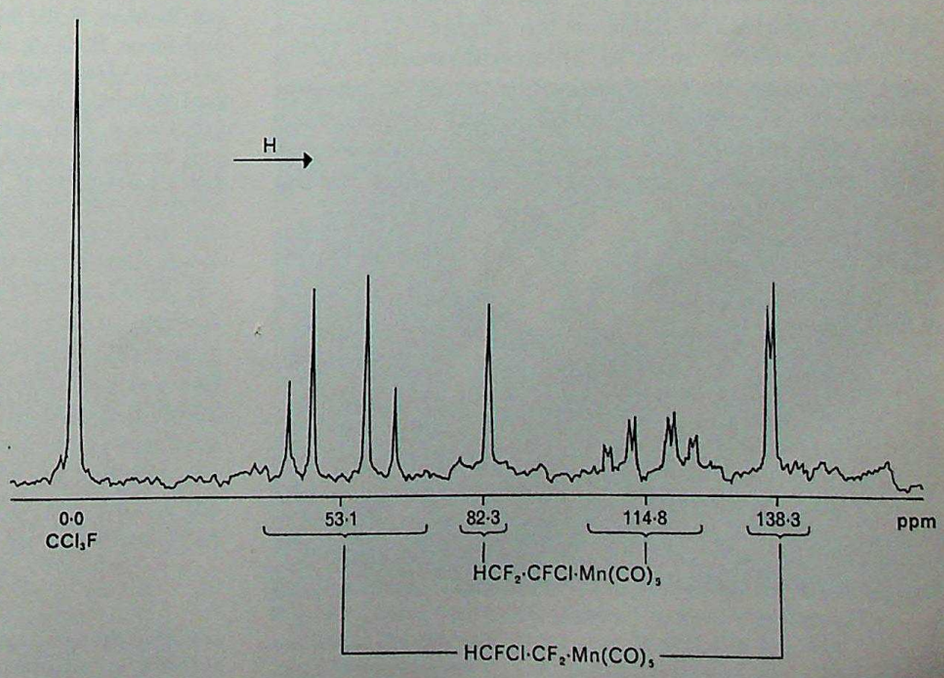


Figure 8 ^{19}F n.m.r. spectra of a mixture of $HCFCl.CF_2.Mn(CO)_5$ and $HCF_2.CFCl.Mn(CO)_5$ from pentacarbonylmanganese hydride and chlorotrifluoroethylene.

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of the two isomeric complexes $HCCl_2CF_2Mn(CO)_5$ and $HCF_2CCl_2Mn(CO)_5$ affords pentacarbonylmanganese chloride. However, solutions of $HCF_2CCl_2Mn(CO)_5$ decompose within a few minutes even at room temperature, thereby enabling $HCCl_2CF_2Mn(CO)_5$, the more stable isomer, to be recovered pure from a mixture of the two. The driving force for these thermal decompositions is undoubtedly the formation of the very stable metal-halogen bonds. The formation of zirconium-fluorine bonds is known to be particularly exothermic, and it is perhaps not surprising that the compound $(\pi\text{-}C_5H_5)_2\text{-}Zr(C_6F_5)_2$ explodes when heated above its melting point (218°C) in air, although it is quite stable up to its melting point. Violent decomposition does not occur, however, when the zirconium complex is melted under nitrogen. The vigour of the decomposition could, therefore, be due to the organic moiety formed, which might perhaps be perfluorobenzyne, if it reacts explosively with oxygen at the elevated temperature needed to initiate fluorine-atom migration.

High-resolution nuclear magnetic resonance spectroscopy has been a very important research tool in determining the structures of fluorocarbon complexes of transition metals. Although known primarily for proton studies, n.m.r. spectroscopy can also be used for molecular structure assignments with fluorine compounds, because of the spin of $\frac{1}{2}$ of the ^{19}F nucleus. The effect is enhanced because fluorine has only one isotope. Moreover, 'chemical shifts' are larger with fluorine atoms than with protons, so that the observed spectra are often more easily interpreted. An early example of the use of the n.m.r. technique was the elucidation of the nature of the two products obtained by heating pentacarbonyliron with tetrafluoroethylene, and dicarbonyl-π-cyclopentadienylcobalt with the same compound. In both cases, a novel heterocyclic compound with a metal atom in a ring of CF_2 groups was obtained, and the observed spectra (figure 7) were in complete accord with the proposed structures.

We have previously referred to the synthesis of fluorocarbon-metal compounds by adding transition-metal carbonyl hydrides to fluoro-olefins (figure 1). When a chlorofluoro-olefin, such as chlorotrifluoroethylene, is used, it is possible for the product to be a complex containing the group $HCFClCF_2$-metal or the group HCF_2CFCl-metal, or a mixture of both possible isomers. With pentacarbonylmanganese hydride, both isomers can be produced, depending on the reaction conditions. That this is so was first demonstrated by ^{19}F n.m.r. spectroscopy, the observed bands corresponding to the presence of a mixture containing both groups (figure 8). This observation stimulated the eventual separation by chromatography of the two isomeric pentacarbonylmanganese complexes.

Conclusion

This review has been concerned with the way that the study of a sub-branch of organometallic chemistry, that concerned with fluorocarbon derivatives, has added to our knowledge of metal complexes. Many new fluorocarbon-metal compounds will be discovered in the future, but it seems likely that future studies will be increasingly concerned with using some of the recently characterized compounds as starting points for further syntheses. It is already evident that attachment of metals to some of the fluorocarbon groups can modify the properties of these groups; it is possible that certain metals will function as templates, enabling new fluorine compounds to be prepared.

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The activity of the mollusc neuron

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Ladislav Tauc

Until recently, it was thought that the neuron, the individual cell of the nervous system, acted as a unit. It has now become clear that this view is oversimplified and that individual neurons can integrate—sometimes by summation, sometimes by restricting the movement of the action potential—the impulses they themselves produce. Some neurons can act as if they were a number of neurons, by affecting in a different manner each of the effectors to which they are connected. This article describes the work that has led to an understanding of these properties.

It was the distinguished anatomist Ramón y Cajal who established in the 1890's [1] that the neurons, the cells of the nervous system, were individual entities and the basic units of the nervous system. His concept was confirmed at the beginning of this century by the discovery of the unit by which the neuron acts, the nervous impulse. This appears as a rapid change of electrical potential that occurs at one point in the neuron and spreads throughout it by exciting the nearby parts so that a wave of potential passes along the cell. This nervous impulse has an 'all or nothing' character, and its magnitude is independent of that of the stimulating impulse.

For a long while, the action of the central (that is, the non-peripheral) neurons was thought to be as follows. There is normally a potential difference—the resting potential—between the inside and the outside of the cell membrane. The impulses from the interneurons or from the peripheral receptors are transmitted to the central neuron through the junctions (the synapses), and the resultant potentials—the excitatory post-synaptic potentials—lower the potential difference across the cell membrane. At first this depolarization spreads along the surface of the cell, which behaves at this stage like a core conductor. The spread is known as electrotonic spread. As the depolarization increases, the neuron ceases to act as a passive core conductor, and eventually a threshold is reached. The nervous impulse, known as the action potential or the spike, is initiated. According to the classical theory, this spike will invade the whole of the neuron and then, through its axon terminals, stimulate other neurons. This picture of the action of the neuron nowadays seems oversimplified. The neuron can be regarded as the unit of nervous function only with considerable reserve, as modern work, particularly during the last ten years, has shown that its action is extraordinarily complex. There are local activities that are not propagated, and some of these are produced spontaneously by an intrinsic 'pacemaker'. In addition, the parts of the cell—the soma, the dendrites, and the axon—differ in their properties, and it is the intrinsic differences, including anatomical differences, between one cell and another that enable each to react in its own individual way in integrating the impulses it receives. It has been found, in addition, that the arrival of the spike at one point of the neuron is not necessarily the end of the integrating process, as the spike can be prevented from invading the whole of the neuron. This activity, in which the spike acts as an integrating element, is the particular concern of this article.

Ladislav Tauc, *Docteur ès Sciences*
Was born in Czechoslovakia in 1926 and educated at the Universities of Brno and Paris. He now directs the cellular neurophysiology laboratory of the Centre National de la Recherche Scientifique at Paris. His principal research interests are in the biophysics of the neuron and in neuronal interaction and integration.

The passage of the spike through the neuron

We intend to answer three questions that are fundamental to neurophysiology. These are:

1. Whereabouts in the neuron does the nervous impulse start?
2. How does the spike propagate from this point?
3. How does the spike act as an integrating agent?

In general, these problems have been studied in the central neurons of vertebrates, particularly the motor neuron of the spinal column of the cat and the frog [2]. This work has suggested that the action potential originates in the axon hillock, the region where the axon joins the soma (zone II in figure 5). However, this has never been directly proved, mainly because it is impossible to see the individual neurons, which are buried in tissue. We used instead the ganglionic neurons of the sea hare *Aplysia*, a marine mollusc, and have been able to make a detailed study of all of these problems [3–5]. The central nervous system of this animal consists of a number of ganglia, and is in many ways particularly suitable for study. While the bio-electric properties of these neurons are essentially the same as those of the vertebrates, the neurons themselves are larger and much easier to prepare. In addition, their location means that one can work under direct visual control; and they are easily identifiable, and thus can be recognized in each of

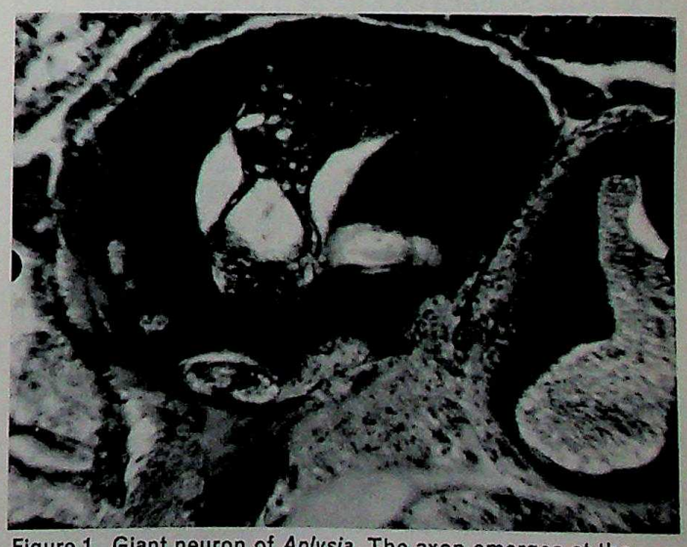

Figure 1 Giant neuron of *Aplysia*. The axon emerges at the bottom of the cell and the nucleus is in the centre. The soma is surrounded by connective tissue and glia. There is another cell body at right (× 200). (By courtesy of Professor T. H. Bullock)

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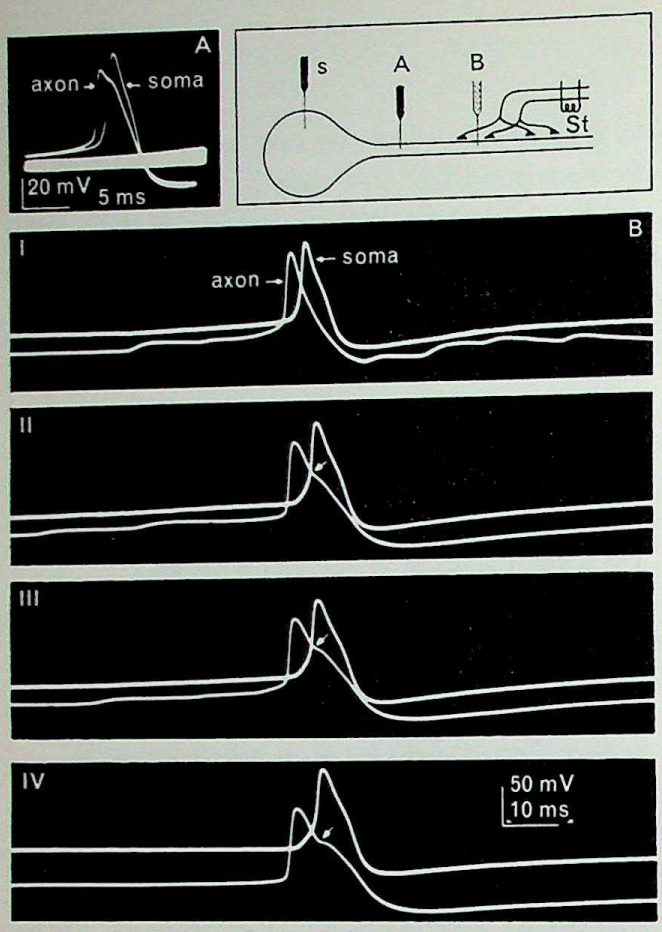

Figure 2 Traces of intracellular potential changes in the soma and axon of the *Aplysia* giant neuron, after orthodromic stimulations. Electrode A (giving figure A) is 300 μ from the soma; electrode B is 2 mm from the soma. Figures B (I) – B (IV) show that repeated stimulation increases the time between the axonal spike and the somatic spike. The somatic discharge re-excites the axon, and the arrows show the start of this excitation. (St = stimulus) [3]

a series of preparations. These properties mean that one can obtain the completely reproducible results that are needed for an intensive study.

The point of origin of the action potential

Most of the experiments have used the giant neuron from the abdominal ganglion. Its soma has a diameter of about 400 μ, and can be as large as 800 μ. As is usual among the molluscs, the soma is round and has no dendrites, and there is only one axonal process, which has no myelin sheath. The neuron is shown in figure 1. It is now known [6] that its axon leaves the ganglion in one of the connections that goes towards the right pleural gang lion, where it divides into branches that innervate the parapodia and the foot—almost all of those of the right side and a part of those of the left; the neuron, however, acts as an interneuron and has no direct motor function.

In our preparations, the abdominal ganglion, with its nerves and connectives, is removed from the animal, fixed to the bottom of a Lucite tank, and covered with seawater, which we have found to be an ideal physiological solution. The giant neuron is then delicately separated from the connective tissue that covers it, and the micro-electrodes are inserted into the soma and into the part of the axon near the soma that is being investigated. These micro-electrodes are made from glass micropipettes with a diameter at the tip of 1 μ, and they contain potassium chloride solution as a conductor. The changes in potential are measured by comparison with a reference electrode dipping into the seawater that covers the neuron; because the resistance of the micro-electrodes is some tens of megohms, an electronic system with an input resistance some thousands of times as great, and a capacitance of no more than a few μμF, must be used to measure these changes. The changes of potential produce two separate traces on a cathode-ray oscillograph, and these are photographed, so that the sequence in time of the events that occur in different parts of the neuron can be studied.

If a micro-electrode is pushed into the cell, it reveals a resting potential of about −55 mV with respect to the potential of the surrounding fluid. The potential is the same in the soma and in the axon near the soma. Orthodromic stimulation—stimulation through the synapses—produces a post-synaptic depolarization that eventually initiates the spike. When the changes in potential are measured simultaneously in the soma and in the axon near to it, the spike is clearly seen to appear in the axon first (figure 2). As figure 2B shows, the post-synaptic potentials can be detected in the axon 2 mm from the soma, but none can be detected in the soma itself; this confirms the anatomical knowledge [7] that the synapses are all on the axon.

However, the fact that the spike starts in this part of the axon is not mainly due to the position of the synapses; the principal reason is that the axon close to the soma has a lower threshold than have any of the surrounding regions. In fact, the spike in the axon always precedes that in the soma, even when it is produced by a current from an electrode inserted into the soma. In the same way, spikes that are produced spontaneously by the pacemaker appear in the axon first, which indicates that the pacemaker itself is in the axon.

Thus there is one region in the neuron that can be more easily stimulated than the rest, and hence acts as a trigger region for the spike. Experiments using electrodes placed in different parts of the axon have shown that this region is some hundreds of microns long, with its centre about 1·5 mm from the soma.

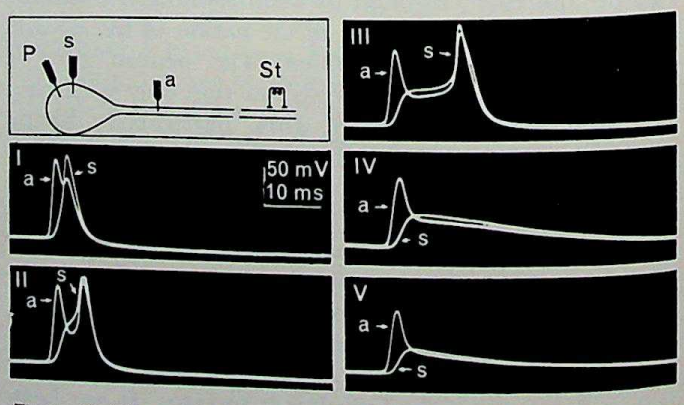

Figure 3 Traces from electrodes in the soma(s) and the axon(a) 700 μ from the soma: antidromic stimulation (st). A polarizing current is applied, in II–V, through P so as to lower the excitability of the cell. The interval between the axonal and the somatic spikes is increased, and the somatic spike is eventually prevented, as shown in IV and V. The electrotonic spread is shown as the same throughout the cell (trace V) because of the low longitudinal resistance between the axon and the soma. Trace IV shows a local response of the somatic membrane to this electrotonic spread. [3]

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The propagation of the action potential along the cell

Figure 2B shows that repeated orthodromic stimulation produces an increase in the time that separates the peak of the spike in the soma from that in the axon. (There is also an increase in the latency of the response, but this is not shown in these figures.) A delay appears in the passage of the spike from the axon to the soma, and the nature of this delay is made clearer in figure 6. Here, a weak hyperpolarizing current is used to reduce the excitability of the cell, and the traces suggest that the first stage of the somatic action potential is actually electrotonic spread from the spike in the axon. It appears as an inflection in the ascending phase of the somatic spike, and is marked 'a' on the lower curves of figure 6. This inflection suggests that there is a discontinuity in the propagation of the spike between the axon and the soma, and that the propagation can be blocked at some definite point outside the soma.

The movement of the spike towards the soma can be better analysed if it is initiated by antidromic stimulation. This is produced by applying an electrical stimulus to the axon a long way from the soma, and without using the synapses (figure 3). This avoids the post-synaptic depolarization that would otherwise reduce the threshold and facilitate the propagation of the spike towards the soma. The spike is propagated entirely as a result of the electrical field that it produces in front of itself. In these conditions, the inflection in the ascending phase of the somatic spike becomes much more pronounced than it was before, and can even appear as a separate wave (figure 3). The first stage is clearly a result of the spike in the axon; the second shows the excitation of the soma. As figures 3 (IV) and 3 (V) show, the spike in the soma can be entirely prevented.

There is thus a region between the axon and the soma where the movement of the spike towards the soma can be blocked. How does this occur? There does not seem

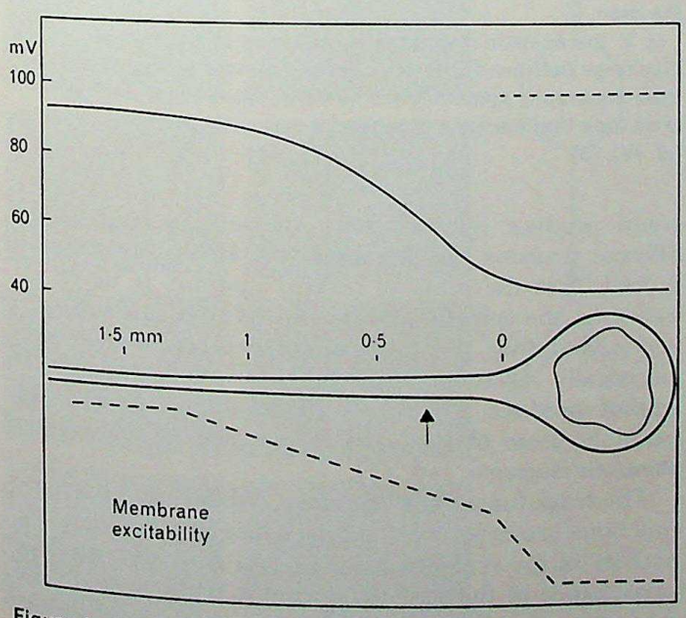

Figure 4 The continuous line shows the amplitude of the axonal spike, antidromically induced, as it nears the soma; resting potential: −60mV. The arrow shows where it is blocked. The upper dotted straight line shows the maximum value of the somatic spike. The lower dotted trace shows, on an arbitrary scale, the change of membrane excitability along the cell. [3]

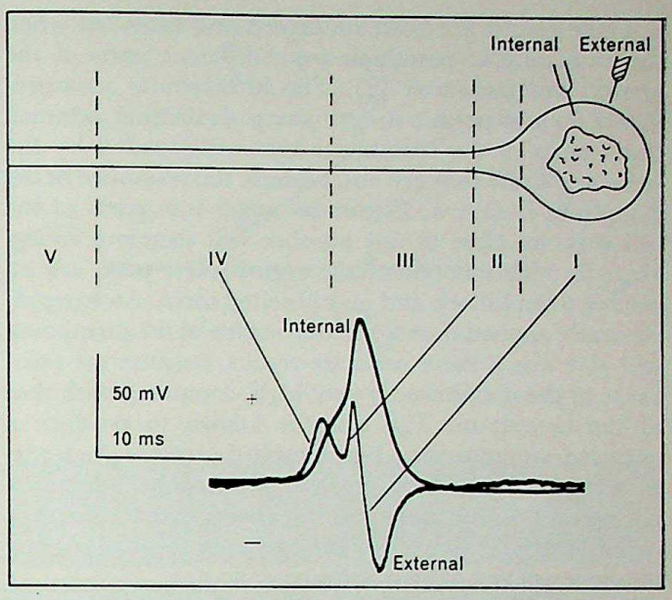

Figure 5 The parts of the cell responsible for the different components of a spike stimulated antidromically. Simultaneous intrasomatic and extrasomatic recordings registered in the soma. (Internal = internal electrode; External = external electrode.) Zone I = soma; zone II = axon hillock; zone III = transition zone; zone IV = the place where the orthodromic spike starts; zone V = the rest of the axon. [4]

to be any anatomical structure that could obstruct the path of the spike, and this suggests that the block is functional. Now the spike is propagated by the depolarization that it produces in the non-excited parts of the membrane, and this membrane has a definite resistance and a definite capacitance. These will affect the magnitude of the spike, and hence its propagation. The unexcited membrane will tend to decrease the magnitude of the spike, and the lower the impedance of this part of the membrane, the more important is the effect of its peripheral shunting. The processes of the nerve are cylindrical, and this limits the capacitance effect; the spike retains an amplitude that ensures its propagation, and indeed with a considerable safety margin. The situation changes completely in the region where the axon enlarges suddenly to join the spherical soma. Here, the impedance of the membrane is markedly decreased because of the large area of the soma, and, as a result, the amplitude of the spike from the axon will also decrease to a size at which it can no longer cause its own propagation. This diminution in the spike has been measured, using electrodes inserted in different parts of the axon near the soma (figure 4).

The spike that has thus been blocked acts electrically on the unexcited somatic membrane. The result is shown on the curves marked 's' in figure 3 (V). The great length of the descending phase is a result of the large time-constant of the somatic membrane, which has to dissipate the charge produced by the axonal spike. The spike blocked in the axon can produce local responses in the soma, as in figure 3 (IV), and these may be sufficiently large to initiate a spike in turn. A comparison of figure 3 with figure 2 shows that the interval between the spike in the axon and that in the soma is shorter for orthodromic stimulation than for antidromic stimulation. This is the result of the facilitation produced by the excitatory postsynaptic potentials.

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These results are both confirmed and extended when the extracellular potentials from different parts of the neuron are measured [4]. The intracellular measurements do not permit a very sharp distinction between those parts of the membrane that are invaded by the spike and those that are not, because the resistance of the cytoplasm is so low. Electrodes going into parts of the cell that are close to one another will therefore record virtually identical potentials, even if these parts are an excited axon hillock and an unexcited soma. An external electrode applied directly to the outside of the membrane will give much more accurate results, because the resistance of the membrane is very high, compared with that of the cytoplasm. The spike is known to produce a negative potential on a closely applied external electrode, with respect to a distant one, and if the external electrode reveals a positive potential, it shows either that the region in contact with it is unexcited, or that it is excited to a lesser extent than a neighbouring one.

Figure 5 shows the picture of the properties of the membrane and of the conduction of the spike that is obtained by a combination of the results from intracellular and extracellular recordings. The giant neuron of *Aplysia* is divided into five zones, each of which contributes towards the potential measured on an internal or an external electrode. The spike is started, either by synaptic action or spontaneously, in zone IV, which has the lowest threshold of the whole cell. The centre of this zone is about 1·5 mm from the soma. The spike is propagated normally in the orthodromic direction (into zone V), but its movement towards the soma is stopped in zone III, because the increase in threshold lowers the safety margin (figure 4), and because the height of the spike is reduced by the shunting effects that we have discussed above. The distance from the soma at which the spike is eventually halted depends on the excitability of the membrane at that particular moment. Normally, an antidromic spike will get as near to the soma as 300 μ, or even 200 μ; but an orthodromic spike will be stopped at the outside edge of the axon hillock. The electrotonic spread from the axonal spike can depolarize zones II and I, and can produce the local response shown in figure 3 (IV). This may start a new spike in zone II that will travel into the soma. This, because of its high threshold, is the last to be excited.

Thus, there is an interruption in the conduction of the spike between the axon and the soma. The spike is transmitted to the soma with a delay whose length depends on the excitability of the neuron at that moment. It is short, and sometimes nonexistent, for an orthodromic spike, but it can last for some tens of milliseconds under certain conditions of excitability. When this occurs, the axon recovers from the refractory state that the passage of the spike has left it in, and is re-excited, this time by the somatic spike, so as to produce a second efferent impulse (figure 6).

As figure 6 shows, an efferent impulse can be produced even if the spike does not reach the soma. As we have said, all the synapses are on the axon, and it should follow that the soma is unnecessary for reflex transmission. It is indeed possible to produce the efferent spike for at least a limited period after the soma has been amputated. An experiment of this type duplicates, with modern methods, the famous experiment of A. Bethe: he showed, as long ago as 1897, that the crab antenna

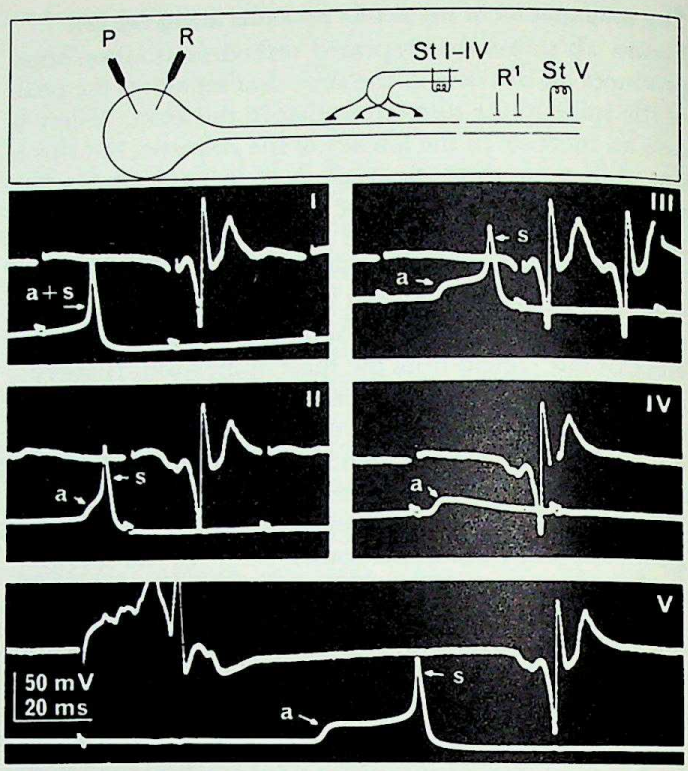

Figure 6 Somatic response to orthodromic stimulation (I–IV) and antidromic stimulation (V). The lower trace is given by the intrasomatic electrode R; the upper by external electrodes (R') 12 mm from the soma. P is a polarizing electrode.

In I, there is no polarizing current. The stimulation produces a somatic spike that is transmitted to the axon.

In II, the polarization is weak. The somatic spike shows two distinct parts, one (a) the result of electrotonic spread from the axon, the other (s) the somatic discharge. The interval separating the (a) surge from its axonal consequence is unaltered.

In III, increased polarization increases the interval between (a) and (s), and each can produce a discharge in the axon.

In IV, a further increase in polarization prevents the somatic discharge. However, the surge (a) can still produce a spike in the axon.

In V, the somatic discharge is produced by the axonal discharge (left-hand side of upper trace) near by that results from antidromic stimulation. The delay between (a) and (s) is so long that the axon is ready for a second discharge (cf. IV). [3]

could produce normal reflex movements even if the afferent neurons had no soma [8]. It has been found, indeed, that the soma of certain neurons is never invaded by the spike in any conditions that can naturally occur, and that the soma of some others is not even electrically excitable [9]. Somatic membranes that cannot produce a spike occur in other neurons, for example those of the cardiac ganglion of the lobster *Panulirus interruptus* [10, 11].

The main function of the soma, other than its trophic functions, seems to be to influence the integration of the activity of the synapses, and it is the resistance and the capacitance of the soma that enable it to do this. The soma can affect the excitatory post-synaptic potentials in the same way as it affects the somatic spike, and the unexcited somatic membrane will markedly diminish their amplitude and reduce their local effects. On the other hand, the capacitance of the membrane extends the time that these potentials last, maintaining them a long time after the disappearance of the activity of the

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transmitter. This activity does not last longer than a few milliseconds, but its influence is so lengthened by the capacitance of the soma that post-synaptic potentials that are separated by tens, or even hundreds, of milliseconds can add their depolarizing phases.

Initiation and conduction of the spike in neurons with branched axons

The axons of nerve cells, as is well known, often contain a number of branches. This enables a neuron to be in contact with a number of other neurons or effectors, and these may be widely spread. So far, we have considered in this article those neurons whose axons branch beyond the synaptic field in another ganglion. However, this is the less common case. In the majority of the central neurons of *Aplysia* and of many other invertebrates, the axon branches before emerging from the synaptic field. The integration of the synaptic effects is then more complicated. It still depends on the local excitability, but it depends also on the geometry of the neuron in the vicinity of the soma and the relative distributions of the synaptic zones along the different branches of the axon.

If we use an electrode inside the soma of certain neurons, we can register a number of surges of potential of different magnitudes, corresponding to the initiation of the spike in different branches of the axon (figure 8 (I)). It is certain that these spikes have not been blocked between the axon and the soma, but by the branches of the axon.

We have used two different methods to study the conduction of the spike from one branch to another [5]. In the more logical method, one branch is stimulated antidromically, using an intrasomatic electrode to show that this has occurred, and the spike is detected in the other branch. However, the branches are normally

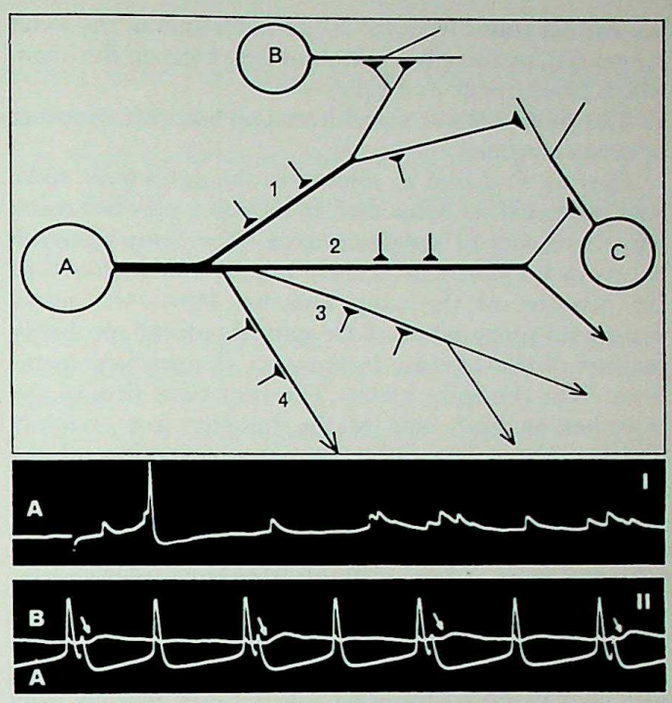

Figure 8 Sketch of a multiply branched neuron (A) from a gastropod.

Trace I shows the intrasomatic surge produced by synaptic stimulation. Some of the branches of the axon have been excited, and these give the multiple discharges and the somatic spike.

Trace II shows simultaneous intrasomatic recordings from neurons A and B. The spikes in A are spontaneous. One axonic branch of neuron A is in contact with neuron B. The excitatory post-synaptic potential (arrowed) appears in neuron B only if the small axonal surge appears in neuron A. The somatic discharge (big spikes) does not invade the axon which synapses on neuron B. Only one in two produces a flux, marked by an arrow, in B. In the other cases, the somatic discharges do not excite the branch of the axon that is connected to B. [5, 14, 3]

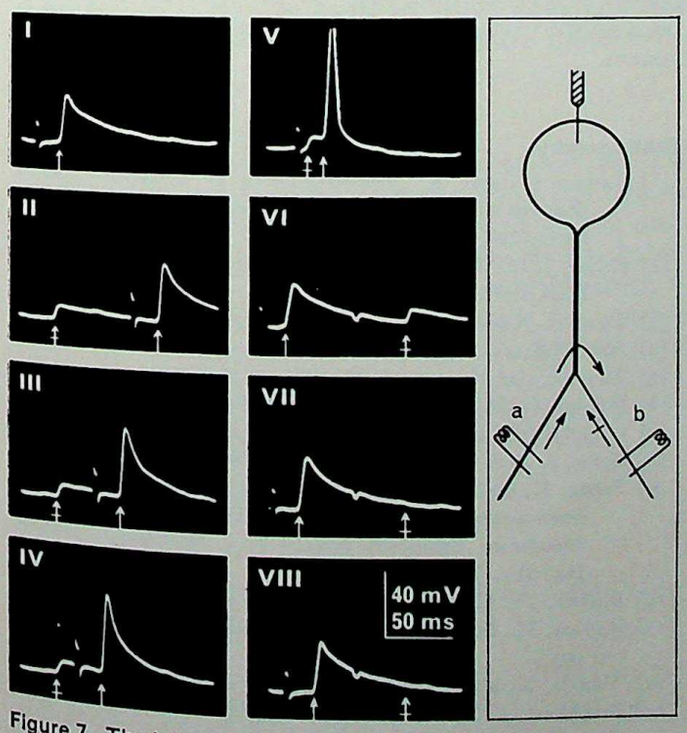

Figure 7 The intrasomatic surges produced by antidromic stimulation of two branches (a,↑) and (b,↑) of an *Aplysia* neuron. In VII and VIII, the spike travels from 'a' to 'b' and prevents the one from giving a result in the soma. In II–V, the spike from 'b' cannot pass the branching, but it facilitates the passage of the other spike, which is therefore larger. [5]

embedded in the nerve and surrounded by thick connective tissue, and must be large if the activity of a single branch is to be distinguished. This method can therefore be used only with certain giant cells. The alternative method is simpler (figure 7). The two branches are both stimulated antidromically at different times. An electrode in the soma detects the effects of the spikes in the axon. If branch 'a' is stimulated first, the conduction of the spike towards branch 'b' can be investigated by stimulating this branch after a delay such that the two spikes will meet in branch 'b' if there is effective conduction from 'a' to 'b'. This is shown in the diagram in figure 7. If an encounter of this type does occur, there will be no somatic surge of potential corresponding to the spike from 'b'. This is the case shown in traces VII and VIII.

We have found that the attempt to send a spike from 'a' to 'b' may produce one of four results.

1. The spike is transmitted from 'a' to 'b', and from 'b' to 'a' by activating a part of the axon (an intermediary zone) which lies between the branching and the soma. The transmission does not need a somatic spike.
2. The spike travels from 'a' to 'b' with the help of the intermediary zone, but a spike from 'b' is blocked before it can excite this zone. The spike can therefore travel in one direction only.
3. The spike travels from 'a' to 'b' by exciting the soma,

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but cannot travel from 'b' to 'a'. Excitation of the soma is essential, as there is no intermediary zone on the axon, which branches at its origin.

4. The spike will not travel from one branch to another in either direction.

Thus we find that in some cells the antidromic spike does not reach the soma and, in addition, may not reach other branches of the same axon. The same situation occurs in the junctions of these branches as we found at the junction of the axon and the soma—the safety margin for propagation of the spike is reduced, probably because of the increase in the area of unexcited membrane that the spike meets. The respective sizes of the branches on each side of the junction are certainly decisive, but it is possible that the excitability of the membrane is lower at the junction than elsewhere.

The initiation of surges of different amplitudes demonstrating the blocking of axonal spikes can be recorded from the soma of some cells after orthodromic stimulation, or even after the stimulation provided spontaneously by a number of pacemakers, as shown in figure 8 (I). A plurality of points where the spike can be initiated has also been proposed for other invertebrate neurons, particularly those of the cardiac ganglion [11] and the abdominal ganglion [12] of the crayfish.

Spikes that are produced orthodromically follow the same rules in their movement towards the soma as do spikes produced antidromically, as we have seen above in at least the giant neurons. Thus a spike that originates in one branch may not travel to other branches of the same neuron. In addition, the spike travels only towards the periphery in the branch in which it was started, whether this initiation was produced synaptically or spontaneously. As a result, as figure 8 (II) shows, it may affect only some of the effectors that it normally innervates. Figure 8 shows diagrammatically a gastropod central neuron and its axons. The excitation of the synapses of one branch can produce a spike in that branch which will travel towards the effectors that it innervates. Thus if the spike is started in branch 1 of the sketch, it will travel towards cell B. The other branches may not be excited, particularly in the absence of any facilitation produced by reactions from their own synapses. It is possible for the electrotonic spread from the axonal spike, added to the synaptic effects, to result in the invasion of the whole neuron by the spike. It is only when the corresponding axonal branch is activated that the post-synaptic potential appears in the post-synaptic neuron B. However, figure 8 (II) shows the case where the somatic discharge, recorded on the lower trace, is unable to invade the whole of the axon.

It is reasonable to suppose that some branches of the axon are preferentially stimulated through particular afferent pathways, and that these, perhaps, correspond to particular functions. Thus J. M. Brookhart and E. Fadiga have shown [13] that, for the spinal motor-neuron of the frog, afferent impulses coming from different regions go to synapses in different parts of the neuron. If our supposition is correct, the afferent impulses from a particular region may excite selectively one branch only of the axon, and the spike that is thus initiated will affect only the structures that this branch innervates. (A similar sequence may result from the spike initiated by an axonal pacemaker.) In this way, a single neuron may respond only partially to stimulation, and sometimes in a markedly directional way, because the branches of the axon often go to different nerves that innervate quite separate effectors after they have left the ganglion.

It now seems clear that the initiation of a spike in one branch facilitates initiation in the others. This is because the electrotonic spread from the potential surge that the spike produces in the soma is added to the depolarization produced synaptically in the branches near the soma, and even in the soma itself. In addition, the electrotonic effects from a number of surges in the soma can act additively, so that the neuron is generally invaded by a spike (figure 8 (I)). The neurons of *Aplysia* can then integrate the direct synaptic activity and also the effects of locally initiated spikes. The way in which each neuron behaves will be determined by its structure, by the distribution of synapses on it, and by the local variations in excitability. A similar pattern has very recently been found for certain ganglionic neurons in the crayfish [12].

If the neuron is thought of as the unit of nervous action, the work we have described shows that some central nerve cells can behave as if they were a number of neurons. There is a certain amount of independence among the different functions of the one nerve cell, which may affect only a fraction of the other neurons, or effectors, to which it is connected. These local actions, in their turn, can act as integrating elements, by amplifying the effect of the synapses. The result of all of these subdivisions of neuronal activity is to reduce the number of neurons that are necessary if the central nervous system is to function, and to provide an important mechanism that enlarges the integrating powers of that system.

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Temperatures of ions and electrons in the ionosphere

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A. P. Willmore

Until relatively recently, it has been impossible to measure the variations in the temperature and concentrations of ions in the upper part of the ionosphere—the layer of the atmosphere that reflects long-distance radio waves. The measurements that rocket-launched satellites have made possible have shown errors in the assumptions about this region. This article discusses the ionospheric processes and shows how they are connected with processes in the surrounding magnetosphere.

The ionosphere is a succession of ionized layers in the Earth's atmosphere that is the reflector for long-distance radio communication, and is connected with electrical storms and the aurora; it lies above the stratosphere. It is clearly important to investigate both its formation and variations in its constitution, but until 1946, the region of the upper atmosphere above the maximum height attainable by instrumented balloons could be studied only by observations from the ground. Together with theoretical investigations, these gave a fairly accurate idea of atmospheric structure up to several hundred kilometres. Above this, the picture became increasingly uncertain as one moved outwards into interplanetary space; moreover, the description of many low-altitude phenomena, such as the aurora, whose origins are to be found at these greater altitudes, was seriously defective. In 1946, the first sounding-rocket experiments enabled direct measurements to be made in the upper atmosphere. Since that time, spacecraft have become steadily more powerful, and new experimental techniques have been devised, so that measurements can be made in the atmosphere, the magnetosphere, and finally in the interplanetary medium itself. With the new studies has come a clearer picture of the structure of these more remote regions and a better understanding of their interrelationships. It may be useful if, before describing this work, we summarize the early views on the atmospheric structure.

The structure of the Earth's atmosphere

At sea level, the atmosphere is a weakly ionized gas. It is dense, in the sense that the molecular mean free path is short in comparison with any natural scale length, such as the scale height defined below, and it is of remarkably uniform composition. Each of these characteristics is greatly modified as we move away from the Earth's surface. The neutral—unionized—constituents are, to a high degree of approximation, in hydrostatic equilibrium: in other words, the pressure at any altitude is governed by the weight of gas supported above this altitude. Consequently, the pressure and also the density ρ fall with increasing altitude h:

$$\rho = \rho_0 \exp(-h/H)$$

where ρ_0 and H are constants. H, which is called the scale height, is given by

$$H = kT/mg$$

A. P. Willmore, *B.Sc., Ph.D.*
Was born in 1930 and was educated at Holloway County School and University College London. Worked at A.E.R.E. Harwell on the Controlled Thermonuclear Reactor Project, and returned in 1957 to University College, where he is now a Reader, to do space research. He worked on the construction of the satellite Ariel 1, and is now taking part in several rocket and satellite experiments.

where T is the temperature, m the mean molecular mass, g the acceleration of gravity, and k is Boltzmann's constant.

Thus, the mean free path changes considerably: it increases with increasing altitude, becoming comparable with the Earth's radius at an altitude which is different at different stages in the solar cycle, but is about 500 km. Above this altitude, the molecules move in elliptic or hyperbolic orbits depending on their velocities. In the case of hydrogen atoms, a significant fraction has sufficient velocity to escape from the Earth, leading to a continuous loss which is replenished by photo-dissociation of water vapour. This type of loss is negligible for relatively heavy gases, such as molecular nitrogen.

An equally marked change takes place in the composition of the atmosphere. Two different processes are primarily responsible for this. One of these is gravitational settling. There are vertical winds that tend to keep the composition constant, but, above 105–110 km, their effect is outweighed by that due to settling. Above this altitude, the number density of each constituent of the atmosphere decreases with the scale height corresponding to its molecular mass, and the decrease is thus most rapid for the heaviest gases, which experience the greatest gravitational attraction. This leads to an increasing predominance of the lighter gases (atomic oxygen, and helium and hydrogen) at high altitudes.

The second process results from the illumination of the atmosphere by the ultraviolet constituent of sunlight. This includes photons of sufficient energy to dissociate molecular oxygen and also to ionize all the atmospheric constituents. At low altitudes, the atomic oxygen produced attaches in three-body collisions to molecular oxygen, forming a layer of ozone with its maximum density near 30 km. Above 100 km, the density is too low for this process to be significant and so there is more atomic than molecular oxygen; this variation is enhanced at greater altitudes by the gravitational separation just described.

The solar photons of sufficient energy to produce positive ions are usually absorbed above 70 km, and this forms the ionosphere. Below 350 km, the ions recombine before they can diffuse the distance of a scale height, and their density distribution is governed by the balance of ionization and recombination processes. This balance results in a general increase of ion or electron concentration with altitude. Above 350 km, diffusion becomes more rapid than recombination, so that the concentration of both ions and neutral constituents now decreases exponentially with altitude. Thus, near 350 km, a maximum concentration of about 10^6 per cm^3 occurs at what is called the 'F-region maximum'. The major ion here is that of atomic oxygen, because oxygen is the major neutral constituent, but the lighter ions of He^+ and

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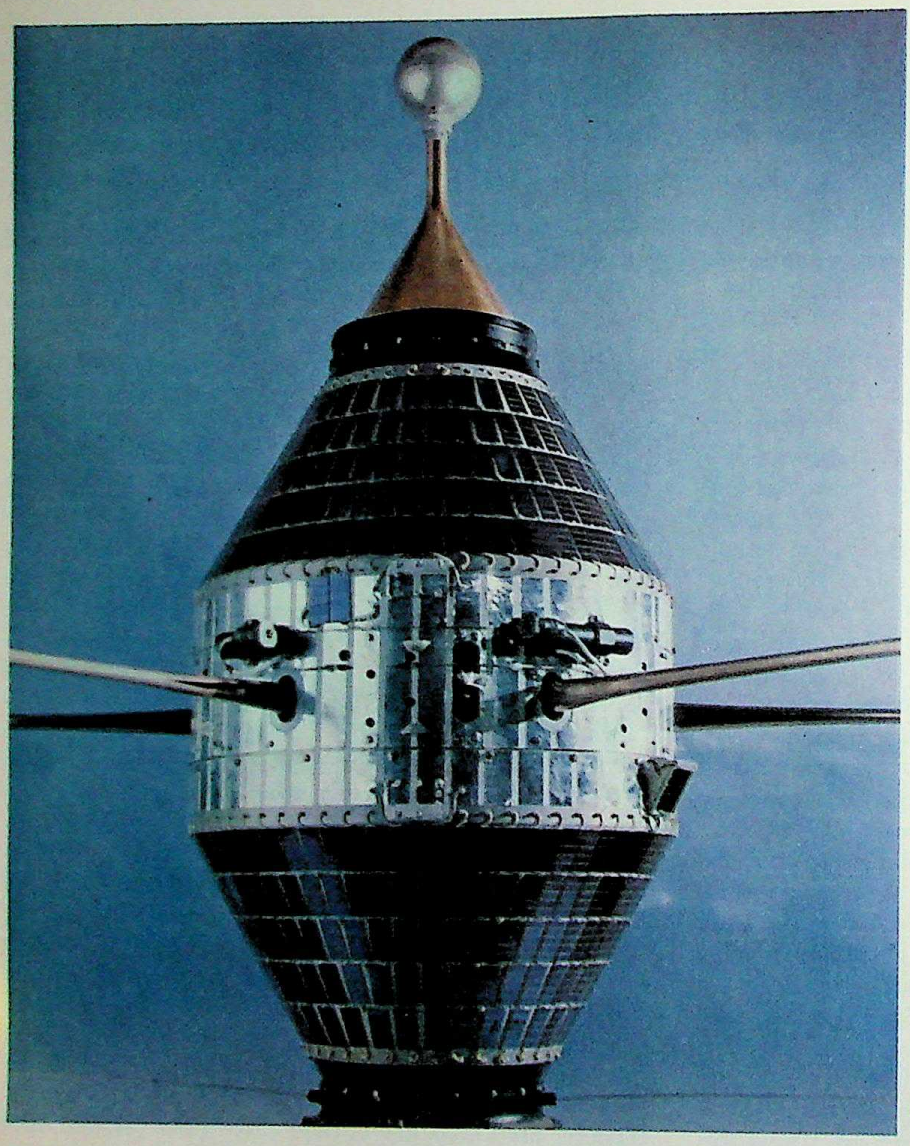
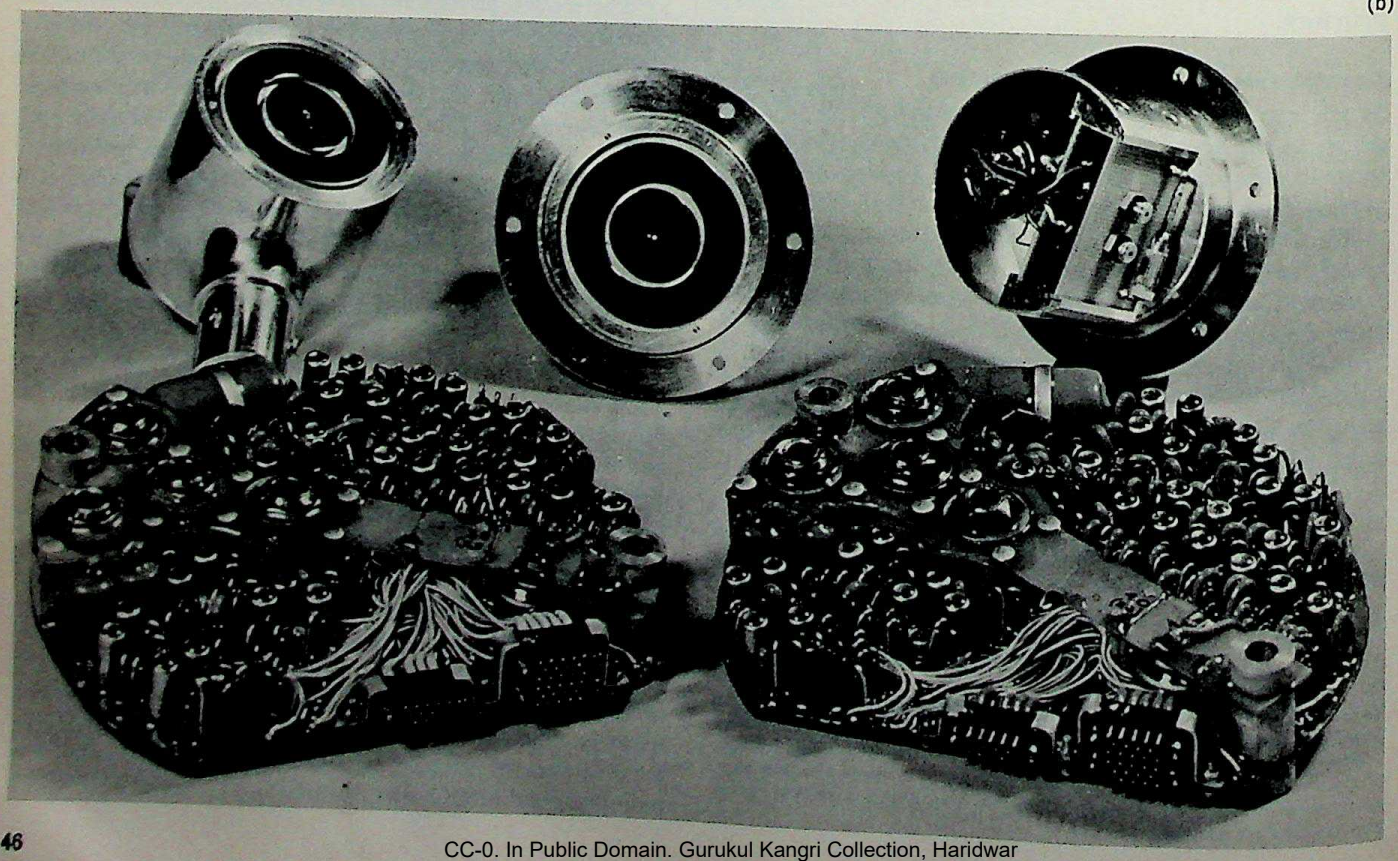


Figure 1(a) This photograph of the Explorer XX satellite shows a positive-ion probe mounted on a short stalk at the upper end.

Figure 1(b) Two electron probes from the satellite Ariel I. The probes are the central disks which are surrounded by guard rings to reduce edge effects. Two sets of electronic equipment are also shown.

(a)

(b)



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H^+ become increasingly important at greater altitudes as a result of gravitational separation.

Above the F-region maximum, there is thus a considerable similarity between the composition and behaviour of the neutral constituents and those of the ionized constituents. There are, however, some important differences. The ionization of an atom results in two particles, one—the electron—of negligible mass, so that the mean mass per particle of the ionized product is only one-half that of the gas from which it is produced. Its scale height is therefore twice as great. So although ionized substances are only a minor constituent (perhaps 10^{-3} in number density) at the F-region maximum, they rapidly increase in relative concentration with increasing altitude, and become the major constituent at several thousand kilometres.

The neutral particles can, of course, move freely across the geomagnetic field, and at high altitudes will travel in the Keplerian orbits already described. The charged particles, on the other hand, must spiral along the field lines in helices of fairly small radius. They are consequently always tied quite strongly to the local field line and, except at the lowest altitudes, are constrained to move along it. Similarly, the conduction of energy takes place primarily in the same direction. Above the F-region maximum and up into the magnetosphere —where the process of diffusion is important—the geomagnetic field therefore exerts a dominating influence on the ionized gases.

The atmosphere and ionosphere below 1000 km have been relatively well explored by rockets and satellites, but conditions at greater heights, where the products of ionization become predominant, are less well known. The ions are protons in concentrations of a few hundred per cm^3, and electrodynamic effects become very important at these heights. The solar wind (a low-density stream of ionized plasma emitted from the solar corona) so deforms the geomagnetic field at distances of 10–20 Earth radii that it is confined within a boundary surface called the magnetopause. This is the outermost extension of the Earth into interplanetary space. Within the magnetopause we have the upper ionosphere, which is usually called the magnetosphere; we shall arbitrarily regard the 1000 km level as the boundary dividing the ionosphere from the magnetosphere.

Some of the very considerable energy of the solar wind is transferred across the magnetopause by processes that are not clearly understood. This results in the production of the major part of the high-energy particles of the van Allen radiation belts, and also of the high-energy electrons that are responsible for the polar auroras. In addition, it is probable here that plasma motions take place across the geomagnetic field lines, inducing electric fields perpendicular to the magnetic field. Because the charged particles can move freely along the field lines, the electrical conductivity along them is very high and they approximate closely to equipotentials. Electric fields generated high in the magnetosphere will thus be transferred down along the lines of force into the lower ionosphere, where they will produce movements of ionized material throughout the ionosphere. The anomalous irregularities in the density of the ionosphere which have long been known and which are still unexplained may reflect movements of ions occurring near the magnetopause. The drift velocities can easily be a few hundred metres per second. Some of this motion would be imparted to the neutral atmosphere by collisions, and may account for the rotation of the atmosphere that has been observed from measurements of the drag of satellites.

Electron and ion temperatures in the ionosphere

The suggestion that the kinetic temperature of the ionospheric electrons might differ from that of the neutral particles was first made by W. B. Hanson. Photo-ionization in the atmosphere gives electrons with a mean kinetic energy of about 10 eV, and these photoelectrons may lose their energy in either of two regimes, roughly depending on whether they are produced above or below 350 km. At lower altitudes, their energy is rapidly randomized by collisions with the ionospheric electrons, raising the temperature of the electron gas above that of the neutral atmosphere. Then the energy is transferred by collisions to the neutral particles, and it is finally removed by downward thermal conduction. At greater altitudes, only a part of the energy is deposited locally in this way. The deposited energy raises the electron temperature, but because the concentration of positive ions at great heights is larger relative to that of the neutral particles than it is lower down, the energy is first transferred to the positive-ion gas by ion-electron collisions, and then to the neutral particles by ion-neutral collisions. Finally, it is conducted downwards, as it is at lower altitudes. In this process, the positive-ion temperature is raised to a value intermediate between the electron and gas temperatures.

At altitudes of about 100 km, where the neutral atmosphere is relatively dense, the removal of the excess energy from the electron gas by collisions is very rapid, and a significant difference between the temperature of the electrons and that of the gas cannot develop. At high altitudes, above 350 km, the absorption of ultraviolet energy is small, so that once again a small temperature-difference may be expected. In between these altitudes, and particularly near 180 km, where the greatest absorption of ultraviolet energy occurs, Hanson predicted a maximum temperature difference of 1000–2000°K between the electrons and the neutral gas. Before we compare this with the results of observations, let us consider how these observations are made.

The measurement of atmospheric and ionospheric temperatures

Atmospheric temperatures at heights above 200 km have generally been deduced from air density values obtained from observations of satellite drag. The atmospheric drag on a satellite near the perigee of its orbit can be calculated from a measurement of the rate of change of its orbital period with time. If a number of satellites with a range of perigee heights is available, the altitude variation of atmospheric density can be found. The atmospheric composition near 120 km, where a condition of diffusion equilibrium occurs, is known from mass-spectrometric studies: this composition can be used as the basis of a self-consistent profile of temperature and mean molecular mass which reproduces the observed altitude variation of density. The method is somewhat indirect, but fortunately many suitable satellites exist for observation, and it is possible to calculate the diurnal variations of atmospheric temperature, and also that resulting from the solar cycle,

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solar activity, and differences in latitude. One extremely important result of these studies is to show that above 400 km, the temperature is only slightly affected by changes in altitude and latitude.

More recently, successful measurements have been made at twilight of the broadening by the Doppler effect of scattered resonance radiation from sunlight in sodium and potassium vapour trails emitted by sounding rockets. The temperatures obtained from the Doppler widths are in excellent agreement with those obtained by measurements of drag.

Ionospheric temperatures may, in principle, be deduced from the variation of concentration with altitude above the F-region maximum, but for a number of reasons, this is not a satisfactory technique. Two other methods have proved more fruitful. One of these is the radar-backscatter technique originally used by K. L. Bowles. In this, a powerful radar beam is directed vertically upwards. The ionospheric electrons act as free scatterers, and the scattered radiation is received and its frequency spectrum is analysed. The total scattered energy per unit volume is proportional to the electron concentration, from which its profile can be obtained. The altitude of scattering is, of course, obtained from the time interval between the emitted and received signals. In addition, the frequency range of scattered radiation is broadened by the Doppler effect caused by kinetic motions of the plasma particles. At the wavelengths normally employed (about 1 m), the line profile depends on the mean thermal velocity of the positive ions, because of collective effects in the plasma, and also on the ratio of the temperature of the ions to that of the electrons. The temperatures of both the ions and the electrons can thus be found.

The second method of measuring the concentration and temperature of atmospheric ions employs the Langmuir probe originally devised for the study of gas discharges. In its most general form, this enables the energy distribution functions of the charged particles to be determined. A Langmuir probe (figure 1) is an electrode that is carried by a rocket or satellite, and exposed to the ionospheric plasma; its voltage-current characteristic is then measured. For example, the current i_e due to the arrival of electrons at a probe of area A maintained at a negative potential $-V_p$ is

$$i_e = i_0(n_e, T_e, A) \exp(-eV_p/kT_e)$$

where n_e and T_e are the electron concentration and temperature and e and k are respectively the electronic charge and the Boltzmann constant. T_e can then be obtained from the exponent, and n_e from the current i_0 at space potential (where $V_p = 0$). This relationship is valid for charged particles of any kind having a Maxwellian energy distribution, provided that the electric field about the probe is such as to retard them.

In the case of ions, however, the spacecraft velocity is not small compared with the mean thermal velocity—it is generally greater than it. The energy distribution is not then nearly Maxwellian, as it is for electrons, and a more elaborate method must then be used. The ionospheric experiments carried by the Ariel 1 satellite and devised at University College, London, used a relationship due to M. J. Druyvesteyn:

$$d^2i/dV_p^2 = \alpha V_p^{-\frac{1}{2}} f(E)$$

where α is a constant which depends on, among other things, the particle concentration, and $f(E)$ $(=f(eV_p))$ is the ordinate of the energy distribution function for particles of energy E.

Thus, if d^2i/dV_p^2 is determined as a function of V_p, the energy distribution curve may be plotted, and the ion or electron temperature determined. The value of d^2i/dV_p^2 can readily be measured by applying to the probe two small-amplitude sine-waves of differing frequencies and measuring the intermodulation components of the probe current: these are proportional to the second derivative in the limit of vanishingly small sine-wave amplitudes. The method is equally valid for charged particles of either sign provided that V_p is of the correct sign to retard the particles. The electron current, which much exceeds the ion current because of the large random velocities of the electrons, can be determined with an unscreened probe to sufficient accuracy, but the positive-ion current must be isolated by means of

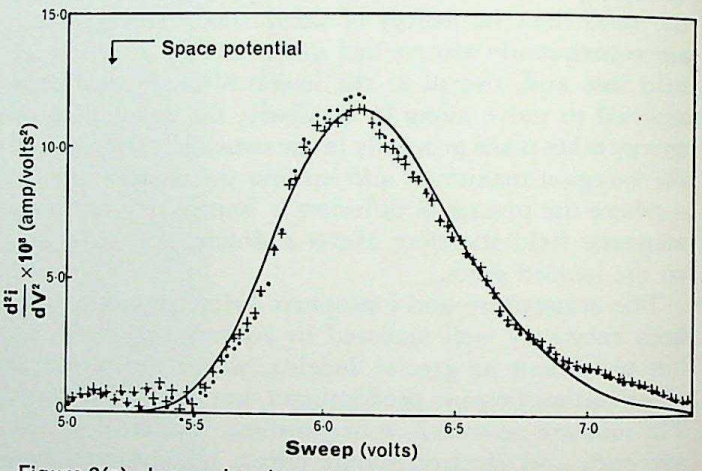

Figure 2(a) Ion probe characteristic obtained from the Explorer XX satellite. This sweep shows a single peak due to He^+ ions. + = observations: · = observations corrected for instrumental broadening: —— = theoretical form of the peak.

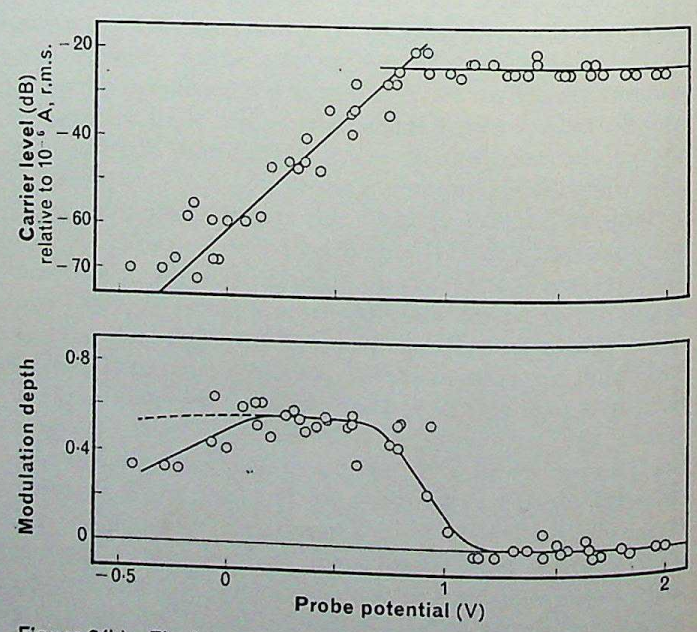

Figure 2(b) Electron probe characteristic obtained on Ariel I. The upper diagram shows probe current increasing exponentially as the probe potential increases. The abrupt change of slope occurs as the probe passes through the potential of the ambient plasma. The lower diagram shows the modulation depth. The broken line indicates the result of applying corrections for instrumental effects.

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a negatively biased screen grid surrounding the probe. Figures 1(a) and (b) show ion and electron probes, and figures 2(a) and (b) show examples of the probe characteristics.

Experiments of this type were carried out by the experimenters using the Ariel 1 and Explorer XX satellites. The electron temperature results from Ariel 1 were particularly interesting because the satellite carried a tape recorder that enabled measurements to be made usefully in the vicinity of ground telemetry stations, and also over the entire orbit. The Ariel 1 results show a good general agreement with radar-backscatter observations for the same period and, moreover, give a far better geographical coverage, so that we can use them for a comparison with the theoretical predictions described in the previous section.

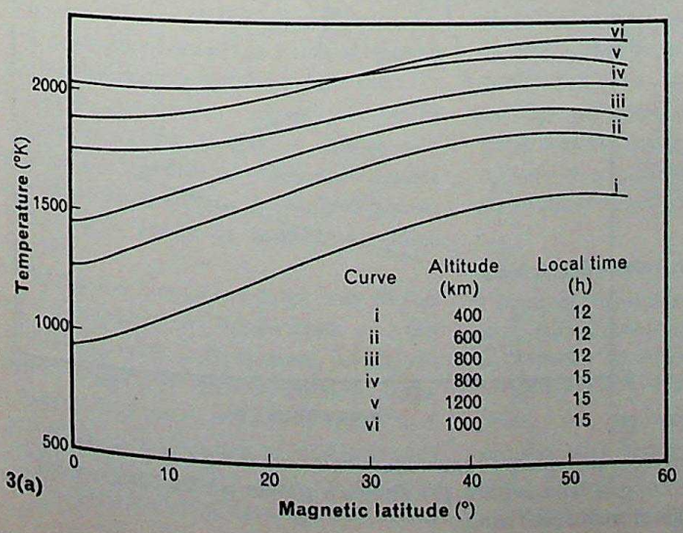
Observed ionospheric electron temperatures

It will be recalled from the previous sections that the temperature of the electrons was expected to differ only slightly from that of the gas above 400 km; and that observations of satellite drag show little variation of gas temperature with altitude or latitude in this region. Thus we should anticipate little variation of electron temperature with altitude or latitude. However, the observations (figures 3 (a) and (b)) show that this is not the case; at least up to latitudes of 60° geomagnetic, and in the altitude range 400–1200 km. This indicates that there is a heat source additional to the photo-electron heating so far discussed. This source has the following characteristics:

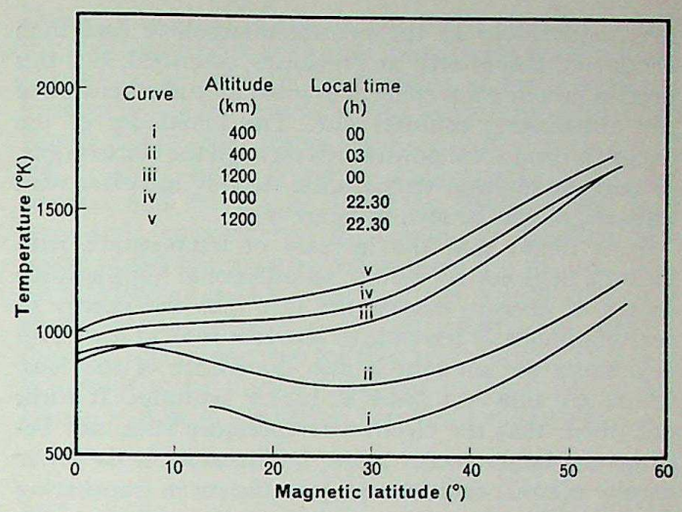
(i) It is effective at least to 1200 km.
(ii) It is stronger at 60° latitude than near the equator.
(iii) It is active by night as well as by day.

It was at first thought that trapped electrons of the van Allen belts were the source, but this is at least partly incorrect. In fact, all the effects observed in the day can be satisfactorily explained by solar heating if an effect neglected in Hanson's original theory is included.

Those photo-electrons produced above 350 km that happen initially to be moving upwards have a good chance of escaping along the geomagnetic field lines into the magnetosphere. As they do so, they will suffer Coulomb collisions with the ionospheric electrons and will so lose a fraction of their initial energy. Energy will be deposited in this way throughout the upper ionosphere and magnetosphere, raising the electron temperature at all altitudes. Part of the energy is passed through



3(a)



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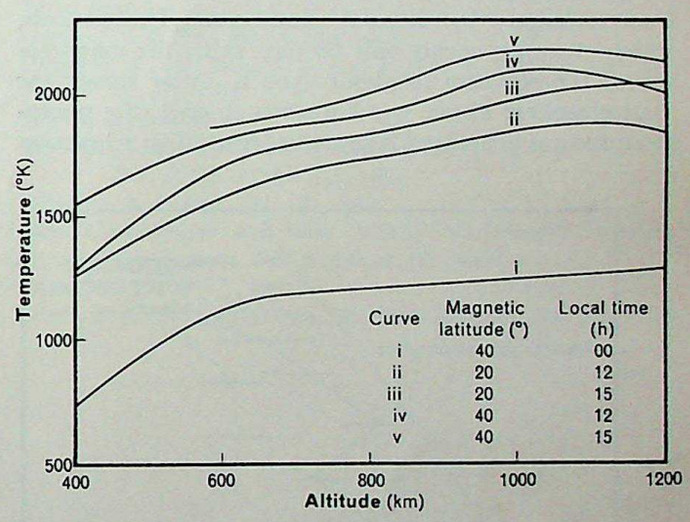
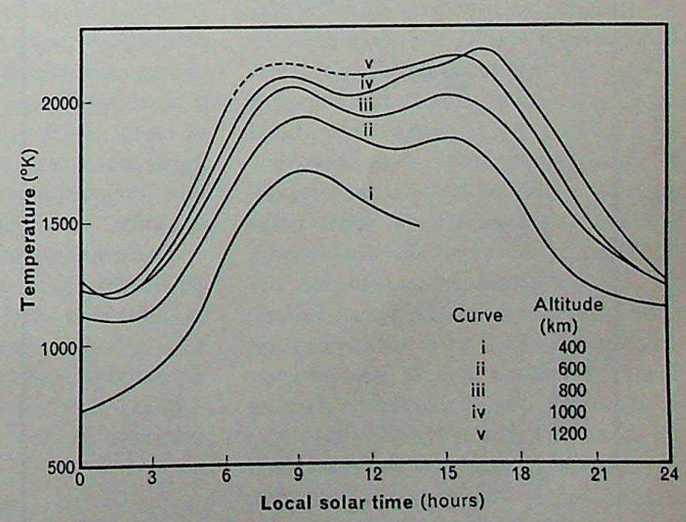


(c)



(d)

Figure 3 Variation of electron temperature in the ionosphere deduced from electron probe measurements made on Ariel I. (a) Variation with magnetic latitude near noon. (b) Variation with magnetic latitude near midnight. (c) Variation with altitude. (d) Diurnal variation at various altitudes and a magnetic latitude of 40°.

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the positive ions to the neutral atmosphere and then conducted downwards as previously described, but this process becomes less efficient at great altitudes because of the diminishing collision rate. The remainder of the energy is conducted downwards through the electron gas, so that the electron temperature steadily increases with altitude, as can be seen in figure 3(c).

It is found that the increase of temperature with latitude does not necessitate an additional high-latitude source of energy, despite the fact that the energy of sunlight is clearly less at high latitudes than at low. This is because the sunlight is also the source of the ions, which are thus less dense at higher latitudes. It turns out, then, that the electron temperature rises, not because of a larger energy input, but because, in the lower density plasma, collisions are less efficient in transferring energy to the neutral gas, and the electron temperature stays high.

We have just seen that a part of the photo-electron energy is deposited in the magnetosphere and removed from it largely by thermal conduction. This process, which of course occurs only by day, raises the magnetosphere temperature to about 3500°K. After sunset the magnetosphere above 350 km starts to cool (the photo-electrons are generated below this level). The relaxation time for this process is about an hour, and the energy thus conducted downwards into the ionosphere must be at least partly responsible for the observed lack of thermal equilibrium in the night-time (figure 3(d)).

However, two other processes have also been suggested by which energy released in the magnetosphere from the solar wind might maintain the electron temperature at night above that of the neutral gas. We have already noted that, near the magnetopause, plasma movements across the geomagnetic field lines may occur, inducing electric fields which are transferred into the ionosphere and produce plasma drifts there. Some part of this ordered drift motion will be randomized by collisions with the neutral atmosphere, raising the temperatures of the ions and electrons. Unfortunately, electric fields of the expected magnitude (10^{-5}–10^{-3} V per cm) are difficult to measure from a spacecraft, so it is not known if these fields exist generally in the ionosphere.

The other heating process that has been postulated is by Coulomb collisions of the relatively high-energy trapped electrons of the van Allen belts. The electrons with energies of many tens of keV which form the best-known constituent of the outer radiation belt are unlikely to have significant ionospheric effects, but it is probable, and there is some confirmatory evidence, that

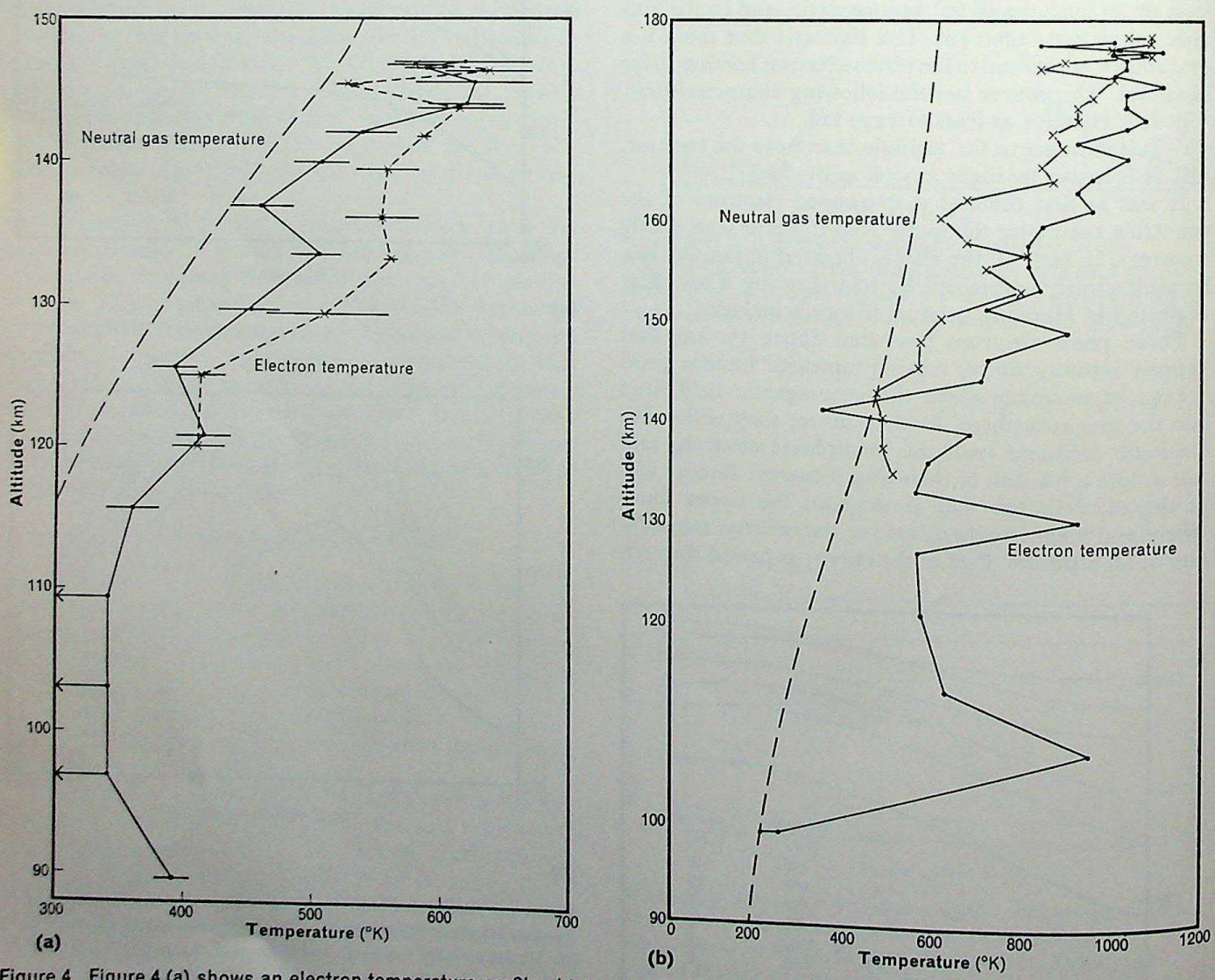

Figure 4 Figure 4 (a) shows an electron temperature profile obtained from a Centaure rocket launched over the Sahara. In the E-region (90–140 km) the electron temperature is essentially equal to the gas temperature. (b) shows a similar profile obtained in a Skylark rocket launched in Sardinia. High and variable E-region temperatures were found.

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these are accompanied by large fluxes of electrons with energies of 1–10 keV or less. Until recently it was believed that these electrons could not penetrate low enough in the ionosphere without producing excessive optical emission from collisions with the neutral particles. This objection is now known to be invalid, and the mechanism is at least a possible one.

Thus, we have three possible processes for maintaining the high electron temperatures of the night ionosphere, each of them involving energy exchange with the magnetosphere. It is probable that the magnetosphere is, at least in parts, a highly turbulent region, although the mechanism generating the turbulence is not understood. Therefore, we may expect the downward energy flux to vary irregularly with position. This will produce corresponding density variations, and because both the energy flux and the particle diffusion occur along the geomagnetic field lines, the irregularities of density will also be aligned along the field lines. Ionospheric irregularities are generally observed to be of this form. Thus, the anomalous form of the upper ionosphere probably reflects the detailed structure of the magnetosphere, of which we as yet know very little. A major objective of future ionospheric research will be the further elucidation of this relationship.

Electron temperatures below the F-region maximum

Electron temperatures in the lower ionosphere, which are measured by experiments using rockets rather than satellites, are rather less well explored than those at greater altitudes. It appears that, from 140 km upwards, Hanson's original picture is essentially correct, though the night-time behaviour near this altitude is not known. On the other hand, in the E-region of the ionosphere, from 90 to 140 km, sporadic high temperatures are often found. Figure 4(a) shows results obtained in a rocket flight when high E-region temperatures were not present, and figure 4(b) shows the results where there were high temperatures—the commoner situation. The origin of the energy required to maintain this temperature difference is unknown, but it is possible that it is ohmic heating produced by the ionospheric currents that are also responsible for such short-period magnetic variations as the diurnal variations, as these currents are known to flow in the region between 100 and 130 km.

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Book reviews

REFERENCE WORKS

Modern Science and Technology, *edited by Robert Colborn, Chief Editor, and the Editors of* International Science and Technology. *Pp. xiv+746. D. Van Nostrand Co. Inc., Princeton, N.J., Toronto, New York and London. 1965. $22.50; £8.*

This book, written mainly for professional scientists and engineers, but comprehensible to the interested layman, aims to acquaint them with the latest discoveries and the state of the art in fields of science and technology other than their own. It consists of articles which originally appeared in the magazine *International Science and Technology*. Although almost all the authors work in the United States, reference is made to workers in other countries.

The subject matter relates only to the understanding or controlling of the physical world and appears under six headings: physics and electronics; technology; chemistry; rocketry, space and astronomy; earth science and oceanography; mathematics and computers. Thus biology, and medical or social science are excluded. Subjects have been chosen for their potential usefulness or development, rather than for the fact that they are well understood or widely used at present, and each article contains a summary and a section recommending further reading. In general the style is refreshingly different from that in learned journals, yet it remains lucid. The book is profusely illustrated with diagrams, photographs and marginal sketches, as well as some colour plates.

The editor is to be congratulated on producing this excellent collection of articles on such diverse subjects. The book is stimulating to read, and deserves a place in any library used by those with an interest in science. *R. B. Whitmarsh*

SEMICONDUCTORS

Chemical Physics of Semiconductors, *by J. P. Suchet (translated from the French by E. Heasell). Pp. xii+197. D. Van Nostrand Co. Ltd, London. 1965. 55s. net.*

When we contemplate semiconductor physics, the sheer virtuosity, technical and theoretical, of what has been achieved in the past twenty years can easily blind us to serious limitations. These are an essentially inward-looking development, and the narrowness of a restriction to only two or three of the simplest materials. These shortcomings result from trying to interpret transport properties in terms comparable with band calculations. If we could relate our experiments to some more flexible, if less rigorous concept we might hope for wider scope. In Dr Suchet's book the potentialities of the chemical bond for this purpose are explored, and we see semiconductor physics expanding to the breadth of chemistry. The author's own contributions to this development are properly emphasized, and the work of others critically appraised. The first steps, taken some ten years ago, now look very primitive in this context; it may be that time will deal as harshly with the more recent work, but this book will retain its value as the first to formalize the subject, and to provide a means of assessing present and future achievements and failures. The chapter on magnetic interactions is particularly timely, and although it is a pity that the treatment

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of charge transport is not better integrated with the rest of the text, this is a small blemish on a useful book. *G. F. Alfrey*

PLASMA PHYSICS

Controlled Thermonuclear Reactions, *by L. A. Artsimovich (translated from the Russian by P. Kelly and A. Peiperl, and edited by A. C. Kolb and R. S. Pease). Pp. xvi+405. Oliver and Boyd, Edinburgh and London. 1964. £5 15s. net.*

The appearance in translation of this survey by Academician Artsimovich should introduce a wide audience to the enormous Russian contribution to controlled thermonuclear research, although the book is not solely an introduction to Soviet work. It is an excellent introduction to the entire field, giving a remarkably clear view of the experimental situation.

This book has the advantage of being the work of an experimenter with wide knowledge, deep insight, and a great deal of common sense. As a result, it escapes the burden of mathematical formalism which tends to encumber the writing of theorists. What mathematics there is is brief, elementary, and close to the physical arguments, themselves cogent and convincing.

The translation has been well effected —well enough to let flashes of the author's pungent wit show through. Altogether the book acts as a satisfactory introduction to the behaviour of stellarators, mirror machines, Theta and Zeta pinches, Alpha and Zeta, and those marvellous monsters Tocomac and Ogra, as well as of the now ubiquitous Joffé bars. *W. B. Thompson*

VACUUM TECHNOLOGY

Fundamentals of Vacuum Science and Technology, *by Gerhard Lewin. Pp. xiii+248. McGraw-Hill Book Co., New York, Toronto, London and Sydney. 1965. 92s.*

The subject of surface phenomena provides a recurrent theme for this book. This is inevitable because, although the whole subject of vacuum science is discussed, emphasis is placed upon the more recent developments in vacuum pumping techniques. For example, nine pages are devoted to diffusion pumps and their baffles, as against nineteen to sorption and ion pumps. This emphasis might be misleading to a student using this text as his first introduction to the subject. Because Dr Lewin has had the benefit of leading a team in a progressive vacuum laboratory, he speaks with considerable authority on those parts of the subject which he emphasizes. The emphasis is therefore to be welcomed.

The actual subjects covered include the relevant parts of the kinetic theory of gases; flow of gases through orifices and tubes; surface phenomena; vacuum pumping and measurements; components and materials; and the techniques of jointing. Considerable practical data of great value to the design engineer are included. A small number of slightly loose statements such as that occurring in the preface, 'One torr is equal to the pressure of a mercury column 1mm height', while unfortunate, do not detract from the value of the book, which can be recommended without reserve to all vacuum technologists. *J. H. Leck*

FRICTION

The Friction and Lubrication of Solids, *Part II, by F. P. Bowden and D. Tabor. Pp. xvi+544. Clarendon Press, Oxford; Oxford University Press, London. 1964. 84s. net (U.K. only).*

Part I of this monograph appeared fifteen years ago and set a standard which few have been able to emulate. Readers might be tempted to criticize Part II on the grounds that there would appear to be gaps in the presentation, but it must be remembered that this book is primarily concerned with the actual work done by the authors and their students: herein lies its authority.

There are very few typographical errors. In figure 104 the valency of molybdenum has been mysteriously halved. On page 218 it is stated that the adhesion of polytetrafluoroethylene (PTFE) to other solids by conventional adhesives is not very satisfactory; this, of course, is not true, as commercial products containing PTFE and resin binder are available which have excellent adhesion to metal and plastic in the air-dried and cured state.

The chapters on solids at high temperatures, friction at high speeds, and liquid impact at supersonic speeds illustrate well how the Cambridge school have kept up to date with newer technologies. For academic workers, the book is a necessity; the industrial appeal is not so great. *E. R. Braithwaite*

CHEMICAL REACTIONS

The Collision Theory of Chemical Reactions in Liquids, *by Alastair M. North. Pp. viii+145. Methuen & Co. Ltd, London; John Wiley & Sons Inc., New York. 1964. 21s. net.*

The collision theory of chemical reactions has been considerably advanced in recent years. It had suffered a certain neglect by reason of the successes of the transition-state theory; but it is the more flexible of the two in dealing with non-equilibrium conditions—for instance, where the rate of reaction is controlled, not by the rate of making or breaking of chemical bonds, but by the rate at which reactant molecules form pairs by diffusion. Many examples of such diffusion-controlled reactions have been discovered in recent years from experimental studies on fast reactions; it is no accident that advances in the collision theory have occurred during the same period. But diffusion theory is also concerned with reactions in general; for it is now generally thought that reactant molecules in solution come together by diffusion to form an 'encounter complex' in which they undergo perhaps 10 to 100 repeated collisions before escaping from the solvent 'cage' in which they are held. Dr North has written an excellent account of the considerable body of theoretical work that has been based on these general ideas. His book is lucid and concise, as befits the series, and can be recommended to all who work on the kinetics of reactions in solution. *E. F. Caldin*

COMPLEX IONS

Stability Constants of Metal-Ion Complexes. *Section I:* Inorganic Ligands, *compiled by Lars Gunnar Sillén; Section II:* Organic Ligands, *compiled by Arthur E. Martell. (Second edition.) Pp. xviii+754. Special Publication No. 17. The Chemical Society, London. 1964. £8 net.*

There is a real problem in reviewing a book of this kind which contains so many original data. Let it be said at the outset that chemists are greatly indebted to Professor Sillén, Professor Martell, and their colleagues, for the enormous amount of hard work which must have gone into the compilation of this volume. They have been very careful to try to include all the apparently reliable data that are available. Although it is pointed out that some attempt to evaluate the data in a critical way has been attempted, one feels that they could perhaps have been a little firmer in rejecting some determinations which they as experts feel do not warrant the same respect as others.

At the present time, there is a rapidly increasing interest in the determination of the heats of complex formation, but there can be no doubt of the importance of free-energy data, such as are provided in this book, for many diverse areas of research in chemistry; thus, in medical chemistry and in analytical chemistry, stability-constant data are essential if

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one is to interpret experimental observations.

The book should certainly be on the shelves of all reputable libraries, but it is hard to see the average chemist buying his own copy unless he needs stability constants in his day to day research activity. The Chemical Society are to be congratulated for arranging to keep this work up to date. *R. S. Nyholm*

MICROANALYSIS

Simultaneous Rapid Combustion. Microchemical Research Papers of Mirra Osipovna Korshun. Methods in Microanalysis. *Vol. I, edited by J. A. Kuck (translated from the Russian by Phyllis L. Bolton and Kurt Gingold). Pp. xv+560. Gordon and Breach, New York and London. 1964. $27.50.*

This work is the first of a series of volumes in which the editor plans to cover methods in microchemistry: and this volume presents methods of organic elemental analysis as developed during the past 25 years by the late Mirra Osipovna Korshun, the noted microchemist of the Soviet Academy of Science, and her co-workers. It consists of translated papers on the determination of carbon and hydrogen, oxygen, nitrogen, the halogens, sulphur, and some other elements present in organic compounds.

Unfortunately, in view of the rapid and valuable developments being made in other countries at the present time, the volume must be regarded as more of historical value than as a textbook for slavish following. Some of the papers appear to be inconsistent with those of workers outside the Soviet Union, but this may be due to translation errors. Because many of the methods presented are now outdated, the value of the volume would have been increased if, instead of merely presenting the verbatim translated articles, the editor had concentrated on presenting a critical review in the light of the more recently published work on organic elemental microanalysis. *G. Ingram*

ORGANIC CHEMISTRY

Dictionary of Organic Compounds, *Fourth edition, edited by J. R. A. Pollock and R. Stevens; originally compiled and edited by the late Sir Ian Heilbron and H. M. Bunbury. Vols I–V and Supplement. Pp. 3492. Eyre and Spottiswoode Ltd, London; E. & F. N. Spon Ltd, London. 1965. £100 the set.*

The publication of this new and revised edition of the Heilbron-Bunbury dictionary is a major event in the world of chemical literature. Especially welcome is the intention to publish regular supplements which will keep the work up to date. The first of these, issued along with the five enlarged basic volumes, covers the literature up to the end of 1964.

The enterprise is a monument to the vision and enthusiasm of the late Sir Ian Heilbron as well as to the industry of the numerous contributors and to the meticulous editorial attention, the results of which are apparent on inspection.

In a project of this size and scope it is necessary to compromise, because the very great number of characterized organic compounds prohibits any attempt at full coverage. Therefore much depends on the wisdom of selections, and it is highly improbable that any two organic chemists or biochemists would arrive at the same, or even similar, conclusions in this matter. However, the saving clause is the provision of supplements, and if anyone feels strongly about omissions, his remedy is to write to the editors. The reviewer wrote down 20 names which he thought should be mentioned and 14 of these were to be found.

Apart from completeness, there are the questions of arrangement and of the matter included under each entry. So far as the former is concerned, the alphabetical system, here adopted, is certainly the best. It requires some attention to nomenclature, and the space devoted to this subject in the introduction, though small enough, probably suffices for the limited objective of guiding the reader.

The choice of material included cannot please everybody, and the references, though extended in comparison with the earlier editions, are still sparse. On the whole a Herculean labour has been courageously tackled, and the result is a set of volumes which will be found essential to organic chemists, and increasingly so to biochemists. *R. Robinson*

ORGANIC COMPLEXES

Molecular Complexes in Organic Chemistry, *by L. J. Andrews and R. M. Keefer. Pp. viii+196. Holden-Day Inc., San Francisco, London and Amsterdam. 1964. $8.75.*

This book begins with a brief introduction to the subject of molecular complexes, encompassing both the carbonium-ion or σ-type and the weaker charge-transfer or π-type. It then turns to the spectra and geometry of these complexes, their stabilities in solution, electrical and magnetic properties, and their functions in organic chemistry. The authors have attempted to consider a wide range of interactions in each section, and the discussion is accompanied by a selection of references giving ample coverage to these interactions and to related phenomena.

The chapter relating to general considerations and the nature of these adducts could well have been expanded, possibly at the expense of the section on complex geometry, and there are a number of errors in the book which could confuse the casual reader. It would also be surprising if all workers in this subject agreed with the conclusions of the authors throughout the book, particularly those discussed in the section dealing with the role of molecular complexes in organic reactions.

The book places special emphasis on those topics which are the authors' own interests, as they admit, but it also provides an adequate background introduction to the subject. *P. G. Farrell*

ALKENE CHEMISTRY

The Chemistry of Alkenes, *edited by Saul Patai. Pp. ix+1315. Interscience Publishers, London, New York and Sydney. 1964. 315s. net.*

Any book devoting 1300 pages to alkenes is obviously a specialist book, primarily for the teacher and the research worker. Nevertheless, much of the material could be very useful to the senior university student.

The book contains 14 chapters by 20 experts. The initial chapter on the wave-mechanical implications of double bonds is followed by three chapters on methods of alkene formation, and seven on the reactions of alkenes and allylic compounds. The final three chapters deal with conjugated dienes, cumulenes, and ketenes.

Two technical features of the book are especially pleasing. The text and figures are very well set out and remarkably free from errors. In a book of this complexity it is cause for congratulation that the references should be up to 1962 and at times even to 1963.

This volume, then, is indispensable as a specialist text, and also as a reference work for senior undergraduates. In welcoming this book we look forward to the promised companion volumes on the carbonyl group, the ether linkage, the carboxyl group, and the nitro group. *P. A. Ongley*

CRYSTALLOGRAPHY

Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959, *edited by L. E. Sutton. Pp. 599. The Chemical Society, London. 1965. 84s.*

The tables to which this book is a supplement were published in 1958, and arose

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from a paper by Allen and Sutton that appeared in *Acta Crystallographica*. So many reprints were asked for that the authors decided that a more extensive compilation was justified. Nearly ten years later the book was published, the result of the work of a considerable team of people.

The present volume brings the subject almost up to date. It contains data based on work by X-rays, electron diffraction, and spectroscopy. There is a table of particularly important bond lengths, elements being listed in alphabetical order of their chemical symbols; then follows the main body of the work—a list of compounds extending over more than 200 pages, giving distances and bond angles in inorganic and organic materials. Lists of references are then given, both by year and journal, in such a way that they can be easily found from the main tables. Finally, there is an index of compounds listed by their names.

The utility of this work cannot be overestimated. All chemists, and crystallographers in particular, need to have access to it. They owe a debt of gratitude to all the distinguished people who have devoted their time to what must have been a dull job, performed entirely for the benefit of their fellow scientists.

H. Lipson

GEOLOGY

Geology, *by William C. Putnam. Pp. xii+480. Oxford University Press, New York. 1964. 55s. net.*

When Professor Putnam of the University of California died in 1963 he had completed the manuscript and drawings for this book. Ten of his colleagues at Los Angeles selected the photographic illustrations and completed the volume as a tribute to the author's memory. It forms a fitting memorial, for it reveals a man skilled in teaching, and also fascinated by the wonders of the earth and able to impart his enchantment to others. Opinion is divided on what should be included in a self-contained one-year University course in so wide a field as geology. This book gives one selection specially suited, as is proper, to students in the Western States of America. From the geological paradises of the National Parks, innumerable magnificent illustrations are drawn; from California, examples of earthquakes and of the birth, development, and future of the oil industry are given. The European geologist will find that physical processes, when viewed from the Western angle, take on almost a new dimension. The treatment is leisurely, almost anecdotal in places, and the book could have been half the size. But then it would have ceased to be the scholarly and entertaining volume that it now is.

H. H. Read

OCEANOGRAPHY

Surface Circulation on the Continental Shelf off Eastern North America between Newfoundland and Florida, *by D. F. Bumpus and L. M. Lauzier. Folio VII of* Serial Atlas of the Marine Environment, *edited by Wilfred Webster. American Geographical Society, New York. 1965. Bound, $8; loose-leaf, $5.*

This very attractive atlas, printed in colour, presents the results of studying the travels of numerous drift bottles recovered from a widely dispersed distribution made over the specified region between 1948 and 1962. In all, 12·7 per cent of the total number (156 276) of bottles liberated were retrieved. Of these, 16 668 (10·7 per cent) were recovered along the U.S. Atlantic seaboard and 356 (2·0 per cent) from overseas stranding places. The fruits of the detailed and valuable study are twelve monthly charts and four seasonal charts which portray the non-tidal drift at the surface on the continental shelf off eastern North America between Newfoundland and Florida. The atlas will be of great use not only to marine scientists, but also to yachtsmen (particularly those who race), to fishermen, to those interested in waste disposal and shore pollution, and to other engineers concerned with shore problems and installations. It has been thought that the monthly and seasonal charts may also serve to settle some heated arguments of importance in fisheries economics, as for instance whether the eggs of inshore lobsters drift offshore or those of offshore lobsters drift inshore.

Authors and publishers alike are to be congratulated upon the appearance of this new folio in the elegant and useful series.

J. N. Carruthers

MORPHOGENESIS

Advances in Morphogenesis, *Vol. IV, edited by M. Abercrombie and Jean Brachet. Pp. x+287. Academic Press, New York and London. 1964. 96s. 6d. net.*

This series continues to provide review articles on developmental biology taken in its widest sense. Exciting problems are raised in a wide variety of systems, and every reader will find some quite new field opened up for him. There is the morphogenesis of the unicellular desmid *Micrasterias* and the problem of 'cytoplasmic axes'; regeneration of lower plants where isolated single cells can give rise to whole plants; the formation of yolk in the hen's egg; and the complex interactions in corneal morphogenesis. The present state of almost all these fields reveals how much still remains to be done, and one must continue to hope for simplifying and unifying principles to emerge.

It is not easy to present reviews of such topics so that the reader who has had little or no previous acquaintance with them can gain insight into them, and many of the articles are very heavy going. However, Gurdon's article on the transplantation of cell nuclei is a model of how this can be done. He helps the reader. His article is also of considerable importance, since he argues that, in general, the results obtained from nuclear transplantation support the view that cell differentiation results from the reversible activation and repression of gene activity, and that this is controlled by the nature of the chromosomal environment.

L. Wolpert

BIOLOGICAL MEMBRANES

Structure and Function in Biological Membranes, *Vol. I, by J. Lee Kavanau. Pp. xiv+321. Holden-Day Inc., San Francisco, London and Amsterdam. 1964. $10.95.*

This is an unusual book, at least as far as can be judged from the first volume. The two volumes together are primarily an exposition of the author's theories on the structure and behaviour of cell membranes. The first volume, however, consists largely of descriptions of work on the physics and physical chemistry of lipids, proteins, water, and their various combinations. These sections in themselves are fairly comprehensive and are useful sources of reference. On the other hand, while the findings of the various investigators have been quite accurately reported, the material is presented uncritically, and in the reviewer's mind, the relevance of much of it to the study of cell membranes is obscure. In fact, the author draws remarkably little on the material in the physical chemical sections to support his ideas on membrane structure.

The theories of membrane structure and behaviour advanced in this volume must be regarded, in our present state of knowledge, as largely speculative. Furthermore, the extent to which they are correct is likely to remain uncertain until much more information is available.

D. A. Haydon

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Structure and Function in Biological Membranes, *Vol. II, by J. Lee Kavanau. Pp. x+760. Holden-Day Inc., San Francisco, London and Amsterdam. 1965. $14.75.*

In the first volume of this work the author postulated a membrane structure of cylindrical lipid micelles. On the basis that this structure is capable of transformations between open and closed configurations, the author here analyses a wide variety of phenomena, which includes cellular movement, membrane dynamics, and active transport. Evidence obtained from the electron microscope for membrane substructure is also considered. In the case of protoplasmic streaming and amoeboid movement, subjects which comprise the bulk of the volume, the basic idea is that membrane-bounded vesicles pump matrix in one direction, while the vesicles themselves are jet propelled in the opposite direction. Microtubules and filaments are regarded as modifications of the membranous system. The treatment is partisan—the interpretations of other workers are largely ignored—and it is often difficult to distinguish between observation and speculation. While the ideas offered are ingenious, there seems very little experimental or theoretical evidence which supports them rather than any of the other current theories. Nevertheless, for the initiated this is a highly imaginative, original, and provocative book.

L. Wolpert

PHOTOBIOLOGY

Recent Progress in Photobiology, *The Proceedings of an International Congress at Oxford, July 1964, edited by E. J. Bowen. Pp. vii+400. Blackwell Scientific Publications, Oxford. 1965. 70s. net.*

This volume is a feat of compression. The scope of the congress included fundamental photochemistry, instrumentation, skin pigmentation, vision, photosynthesis, and radiation damage, and yet the content of 234 papers is presented in 375 pages of text.

Half the text is devoted to nine lectures by such eminent scientists as Terenin, Wald, and Calvin, who each introduced the appropriate session. The lecturers were free to discuss their current interests in photobiology, to relate these to other work, and to speculate. This is valuable reading for specialists and for students of photobiology. Published separately, it would have made an excellent companion to 'Essays in Biochemistry'.

The remaining pages constitute an experiment in scientific journalism that does not merit repetition in this form. The aim was that a session rapporteur, assisted by a discussion secretary, should convey the salient points of the meeting as an account of recent progress. However, to distinguish progress from activity requires time, familiarity with the data, and considered opinion. The reader too often gains only a glimpse of forthcoming work, without having details of the title, publication date, or journal. Unlike those at the congress, he cannot consult the original source of information for elucidation or an independent appraisal, and has only the brief words of the rapporteur. It is, in addition, a pity that there has been a twelve-month delay in publication.

A. P. Brown

DERMATOLOGY

The Epidermis, *edited by W. Montagna and Walter C. Lobitz, Jr. Pp. xx+649. Academic Press, New York and London. 1964. $15.*

Recently a closed meeting was held at Lake Arrowhead, under the aegis of the University of California, where several eminent scientists from various countries discussed the epidermis, giving special attention to keratinization, but also including in their syllabus some references to blistering, psoriasis, cancer, and the metabolism of lipids, carbohydrates, and steroids. Fortunately (for recently we have heard so much about it) they did not consider melanogenesis. This book is an account of the meeting.

The book is well illustrated, chiefly with photomicrographs, and well produced, and must be regarded as a necessity for many physiologists, biochemists, pathologists, and dermatologists.

The editors stated that this is probably the first of a series on the biology of the skin: if they can maintain in each volume the very high standard of excellence that has been achieved in this one, they will produce important source books and we may even become enthusiastic supporters of the idea of the closed conference.

R. M. B. McKenna

PLANT TAXONOMY

Genera of Flowering Plants, Dicotyledons, *Vol. I by J. Hutchinson. Pp. vii+516. Oxford University Press, London. 1964. 126s.*

This is a work of great scholarship which begins a series which will be the modern English equivalent of Bentham and Hooker's *Genera Plantarum* (1862–1883). This is now inevitably out of date, but is the basis of the work under review, which will be welcomed by all concerned with the taxonomy of flowering plants. The basic material consists of family and generic descriptions with critical bibliographical data, information on morphology and anatomy, and discussion of the criteria used in classification. At the generic level, the type species is designated, and the number of species and their distribution are given. The descriptions are lucid and concise, and the keys appear to work well. The necessary inclusion of information which was not available to Bentham and Hooker has led to considerable rearrangement of the genera into tribes and sub-tribes, the number of which is increased, with a welcome gain in clarity and reduction in the number of exceptions. The arrangement of the taxa is determined by the author's controversial interpretation of phylogenetic principles. The chief defect of his classification (which may not affect its usefulness) is that it draws on only a selection of modern work for support. This is a fault inherent in the one-man approach to a vast and intricate subject. However, the advantages of Hutchinson's unique mastery of his material are seen in the circumscription of genera, a field in which breadth of experience and tolerance are essential. The author's expressed hope is that his work will stimulate the production of regional floras and monographs. Their authors are bound to be in Hutchinson's debt, whether they agree with his concepts or not.

D. J. Carr and S. G. M. Carr

MARINE BIOLOGY

Advances in Marine Biology, *Vol. II, edited by F. S. Russell, Pp. x+274. Academic Press, London and New York. 1964. 57s. 6d.*

One of the interesting papers in this book deals with the unsuccessful fish farming of the nineteenth century: newly hatched fish larvae were released in the sea, where they were eaten. The author, Shelbourne, avoids such mortality by keeping large quantities until after metamorphosis: 60 per cent survive. The fish were fed on *Artemia* nauplii and the water was purified with algae, ultra-violet light, and antibiotics; many were abnormally pigmented at high density. The author hopes to increase natural recruitment, develop new nursery grounds, and encourage pond culture of sea fish.

In another paper, J. E. Cushing describes the genetics of blood groups and the separation of subpopulations. Sardines, herrings, trouts, and tuna have been split in the subgroups, and it has been found that yellowfin sera react with human B agglutinogen. A succinct account of experimental methods is given.

Marine bacteriology is the subject of

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the paper by Scholes and Shewan, who describe the oceanic distribution of bacteria from Kriss. They were unlucky that Sorokin did not publish his severe critique of Kriss's methods until June 1964, and their account of it appears in the addendum. The forms of marine bacteria are described together with those associated with net deterioration and fish spoilage.

Another good paper is concerned with methods of sampling of benthos. Holme describes the machines and instruments used, together with the techniques of ship handling, and the statistics that are needed. The account is competent and well illustrated.

The standards of production of the entire volume are good, with clear figures, good plates, and a full index.

D. H. Cushing

INSECT PHYSIOLOGY

The Physiology of Insecta, *edited by Morris Rockstein. Vol. II, pp. xvi+905. 235s. net. Vol. III, pp. xiv+692. 178s. 6d. net; subscription price, 164s. net. Academic Press, New York and London. 1964.*

As in the first volume of this work, the sequence of the topics follows a logical plan devised by the editor, but each chapter is in fact a self-contained entity and can be read independently. That is doubtless how this work of reference will be used.

Many of the chapters in the second volume are excellent. It is remarkable how changed is Pringle's presentation of 'insect flight' since his monograph published in 1957. Four chapters have been translated from German, and some of the authors of these have been more fortunate than others in their translators: the physiology of insect behaviour by Lindauer and Markl must have been good in the original, but it is almost unreadable as printed. But Lindauer on social behaviour and mutual communication is more satisfactory, as are Nachtigall on swimming and Huber on neural integration. Other chapters are by Johnson on migration, Hughes on terrestrial locomotion, and Hoyle on neural control of skeletal muscles. The biochemical chapters by Maruyama on contractile elements of muscle, Sacktor on respiratory metabolism of muscle, Chefurka on intermediary metabolism of carbohydrates, lipids, and nitrogenous compounds, and House on nutrition and digestion cover the greater part of insect biochemistry.

The final volume consists of eleven contributions by different authors. They deal with the insect cuticle, the respiratory system, the haemolymph, excretion, immunology, and resistance to insecticides. Michael Locke provides an imaginative account of recent advances in our knowledge of the integument, many of them due to the author himself. R. H. Hackman who deals with the chemistry of cuticle has been responsible for much original work on the association of protein and chitin, and W. E. Ebeling who writes on cuticle permeability has done outstanding work on the action of sorptive dusts. One of the most thoughtful chapters is that by R. H. Stobbart and J. Shaw on excretion and osmoregulation. M. Florkin and C. Jeuniaux furnish exhaustive data on the composition of the blood; C. Grégoire on coagulation; and J. Colvard Jones on the haemocytes. The critical discussion of immunological responses to micro-organisms and metazoa by J. D. Briggs is most timely; the gigantic literature of the past twenty-five years on insecticide resistance is well handled by A. S. Perry and so is the subject of respiration, by P. L. Miller and by M. Keister and J. Buck. All the chapters are of a high standard. *V. B. Wigglesworth*

HISTORY OF SCIENCE

Cooke and Wheatstone and the Invention of the Electric Telegraph, *by Geoffrey Hubbard. Pp. ix+158. Routledge and Kegan Paul, London. 1965. 21s. net.*

In spite of the author's claim that he is 'a scientist by training . . . and not . . . a proper historian' this is a history book, primarily the story of Cooke and Wheatstone with the telegraph as their background. Mr Hubbard has had access to the manuscript papers of both men, and has been able to throw light on the two strange complementary personalities who combined to produce the working telegraph in England. Yet these two great men allowed petty quarrels over priorities to spoil their friendship. Even after Mr Hubbard's work, their separate characters are not clear-cut; Wheatstone, the theorist with an understanding of Ohm's law (he read German), was able to bring Cooke's dream to reality; Cooke, the businessman and practical engineer, bargained with directors of the new railway companies. Yet Wheatstone had the dexterity to build beautiful terminal equipment, such as the A.B.C., and the punched-tape automatic sender—apparatus in use for a century. Also, Wheatstone drew such financial benefit from the partnership that he left a considerable fortune; Cooke died in poverty.

The book is packed with information and is a pleasure to read, and the anecdotes are delightful. *E. A. Marland*

Michael Faraday, a Biography, *by L. Pearce Williams. Pp. xvi+531. Chapman and Hall, London. 1965. 70s. net (U.K. only).*

This excellent new study of Faraday's life and work by Professor L. Pearce Williams takes its place at once as the standard biography of one of the most remarkable experimenters in the long record of scientific research. Its fascinating detail is based on Faraday's published work, and also on manuscript sources, letters, and other documents, traced to many libraries and other sources and all studied with a scholarly industry that befits its great subject. From Faraday's descent and family connexions the author passes on to relate the details of his early life and education, or self-education, scientific and philosophical, until his entry to the Royal Institution as laboratory assistant brought him into almost daily contact with Davy. Thereafter Faraday's genius steadily revealed itself, as Professor Williams shows, with a brilliance that has never faded even among his more recent successors in experimental physics. The chapters here devoted to the discovery of electromagnetic induction, to the nature of electricity, to the correlation of forces, and to the origins of field theory are of special interest for their detailed critical presentation. Well illustrated and indexed, and fully documented, this biography is a model of its kind.

Douglas McKie

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Some books received

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(*Note.* Mention of a book on this page does not preclude subsequent review.)

MATHEMATICS

Classical Mechanics, *by D. E. Rutherford. (Third edition.) Pp. viii+206. Oliver and Boyd Ltd, Edinburgh and London. 1964. 10s. 6d.*

Cumulative Sum Techniques, *by R. H. Woodward and P. L. Goldsmith. Pp. viii+66. Mathematical and Statistical Techniques for Industry: ICI Monograph No. 3. Oliver and Boyd Ltd, Edinburgh and London. 1964. 18s.*

Integral Calculus, *by W. Ledermann. Pp. viii+85. Routledge and Kegan Paul Ltd, London. 1964. 5s.*

Mathematical Trend Curves: An Aid to Forecasting, *by J. V. Gregg, C. H. Hossell and J. T. Richardson. Pp. viii+99. Mathematical and Statistical Techniques for Industry: ICI Monograph No. 1. Oliver and Boyd Ltd, Edinburgh and London. 1964. 18s.*

Short-term Forecasting, *by G. A. Coutie, O. L. Davies, C. H. Hossell, D. W. G. P. Millar, and A. J. H. Morrell. Pp. viii+36. Mathematical and Statistical Techniques for Industry: ICI Monograph No. 2. Oliver and Boyd Ltd, Edinburgh and London. 1964. 12s. 6d.*

PHYSICS

Curiosities of Light Rays and Light Waves, *by S. Tolansky. Pp. vii+109. Veneda Publishing Co. Ltd, London. 1964. Cloth, 21s.; paper, 12s. 6d.*

Fundamentals of Transmission Electron Microscopy, *by Robert D. Heidenreich. Pp. xiv+414. John Wiley & Sons Inc., New York, London, and Sydney. 1964. 109s.*

Initiation à la théorie de la relativité, *by Vladimir Kourganoff. Pp. 179. Presses Universitaires de France, Paris. 1964. 12 Frs.*

Lectures on Magnetoionic Theory, *by K. G. Budden. Pp. 82. Gordon and Breach, Science Publishers Inc., New York. 1964. Cloth, $3.95; paper, $1.95.*

Progress in Infrared Spectroscopy, *Vol. II. Edited by H. A. Szymanski. Pp. 298. Plenum Press, New York. 1964. $12.50.*

Strong-interaction Physics – A Lecture Note Volume, *by M. Jacob and G. F. Chew. Pp. xi+154. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $9.90; paper, $5.45.*

Symmetry in the Solid State, *by R. S. Knox and A. Gold. Pp. xii+344. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $11; paper, $6.55.*

Ultrasound – Physical, Chemical, and Biological Effects, *by I. E. El'piner (translated from Russian by F. L. Sinclair). Pp. viii+371. Consultants Bureau Enterprises Inc., New York. 1964. $22.50.*

CHEMISTRY

Chemical Binding and Structure, *by J. E. Spice. Pp. xiii+395. Pergamon Press Ltd, Oxford. 1964. 21s.*

The Chemical Constitution of Natural Fats, *by T. P. Hilditch and P. N. Williams. (Fourth edition.) Pp. xv+745. Chapman and Hall, London. 1964. 150s.*

Molecular Orbital Theory, *by C. J. Ballhausen and H. B. Gray. Pp. ix+273. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $9.90; paper, $5.45.*

Molecular Structure, *by K. R. Jennings. Pp. viii+128. Chapman and Hall, London. 1964. 10s. 6d.*

Organic Chemistry for General Degree Students, *Vol. I:* Fundamental Aliphatic Chemistry, *by P. W. G. Smith and A. R. Tatchell. Pp. viii+292. Pergamon Press Ltd, Oxford. 1965. 25s.*

Polymers: Structure and Bulk Properties, *by Patrick Meares. Pp. xi+381. D. Van Nostrand Co. Ltd, London. 1965. 70s.*

Proceedings of the Third International Congress on Catalysis, Amsterdam, 20–25 July 1964. *Vols. I and II. Edited by W. M. H. Sachtler, G. C. A. Schuit, and P. Zwietering. Vol. I: pp. xv+762. Vol. II: pp. viii+763–1445. North-Holland Publishing Co., Amsterdam. 1965. 320s.*

Solubilities of Inorganic and Organic Compounds. *Vol. II, Part II:* Ternary and Multicomponent Systems. *Edited by H. Stephen and T. Stephen. Pp. 947–2053. Pergamon Press Ltd, Oxford. 1964. £12 10s.*

Transition Metal Compounds: Transport and Magnetic Properties. *Edited by E. R. Schatz. Pp. vii+136. Gordon and Breach, Science Publishers Inc., New York and London. 1964. Cloth, $9.50; paper, $5.*

GEOPHYSICS

Solar Plasma, Geomagnetism and Aurora, *by Sydney Chapman. Pp. 141. Gordon and Breach, Science Publishers Inc., New York and London. 1964. Cloth, $4.95; paper, $1.95.*

BIOLOGY

Advances in Radiation Biology, *Vol. I. Edited by L. G. Augenstein, R. Mason, and H. Quastler. Pp. x+285. Academic Press Inc., New York and London. 1964. 88s.*

Cybernetics and Biology, *by F. H. George. Pp. viii+138. Oliver and Boyd Ltd, Edinburgh and London. 1965. Cased, 21s.; paper, 12s. 6d.*

Electron Microscopic Anatomy. *Edited by Stanley M. Kurtz. Pp. xii+425. Academic Press Inc., New York and London. 1964. 100s.*

International Review of Connective Tissue Research, *Vol. II. Edited by D. A. Hall. Pp. xiii+350. Academic Press Inc., New York and London. 1964. 93s.*

An Introduction to Microbiology, *by W. B. Hugo. Pp. ix+146. Pharmaceutical Monographs, Vol. I. William Heinemann Medical Books Ltd, London. 1965. 20s.*

Isotopes in Biology, *by George Wolf. Pp. x+173. Academic Press Inc., New York and London. 1964. Cloth, $5.50; paper, $2.45.*

The Molecular Basis of Heredity, *by A. R. Peacocke and R. B. Drysdale. Pp. viii+180. Butterworth & Co. (Publishers) Ltd, London. 1965. 37s. 6d.*

Normaler und hoher Blutdruck und kardiovaskuläre Mortalität bei verschiedenen Völkern, *by Robert Stigler. Pp. xii+294. Dr. Dietrich Steinkopff Verlag, Darmstadt. 1964. Cloth, 94 DM.*

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Theory and Practice in Experimental Bacteriology, *by G. G. Meynell and E. Meynell. Pp. xii+287. Cambridge University Press, London. 1965. 50s.*

BIOCHEMISTRY

Animal Hormones, *by J. Lee and F. G. W. Knowles. Pp. 192. Hutchinson University Library, London. 1965. 15s.*

Biochemistry and Behavior, *by S. Eiduson, E. Geller, A. Yuwiler, and B. T. Eiduson. Pp. xii+554. D. Van Nostrand Co. Ltd, London. 1964. 116s.*

Biochemistry and Physiology of Protozoa, *Vol. III. Edited by S. H. Hutner. Pp. xiv+616. Academic Press Inc., New York and London. 1964. 132s.*

Essays in Biochemistry, *Vol. I. Edited by P. N. Campbell and G. D. Greville. Pp. xi+170. Published for the Biochemical Society by Academic Press Inc., London and New York. 1965. 18s. 6d.*

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Biogéographie végétale, *by P. Ozenda. Pp. 374. Editions Doin, Paris. 1964. 45 Frs.*

The Plant Cover of Sweden. *Pp. 314. (Acta Phytogeographica Suecica, Vol. 50.) Societas Phytogeographica Suecana, Uppsala. 1965. Cloth, Sw. Kr. 87; paper, Sw. Kr. 72.*

Spores, Ferns – Microscopic Illusions Analyzed. *Vol. I:* Varied Plant Groups Introduce True Ferns through Spore Tetrad Structure, *by Clara S. Hires. Pp. xxiv+548. Mistaire Laboratories, Millburn, N.J. 1965. $22.50.*

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Animal Nutrition, *by Cyril Tyler. Pp. xii+253. Chapman and Hall, London. 1964. 28s.*

The Biology of Hemichordata and Protochordata, *by E. J. W. Barrington. Pp. vi+176. Oliver and Boyd Ltd, Edinburgh and London. 1965. Cased, 25s.; paper, 15s.*

Marine Mammals, *by R. J. Harrison and J. E. King. Pp. 192. Hutchinson University Library, London. 1965. 15s.*

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The Grassland and Fodder Resources of India, *by R. O. Whyte. Pp. x+553. Indian Council of Agricultural Research, New Delhi. 1964. Rs. 20.*

ENGINEERING

High Voltage Direct Current Convertors and Systems. *Edited by B. J. Cory. Pp. xiii+269. Macdonald & Co. (Publishers) Ltd, London. 1965. 55s.*

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Rechtfertigung und Bericht über meine Reisen in verschiedene Orte, *by Ambroise Paré (translated from French by E. H. Ackerknecht). Pp. 125. Verlag Hans Huber, Berne and Stuttgart. 1963. Cloth, 22.50 DM.; paper, 7.50 DM.*

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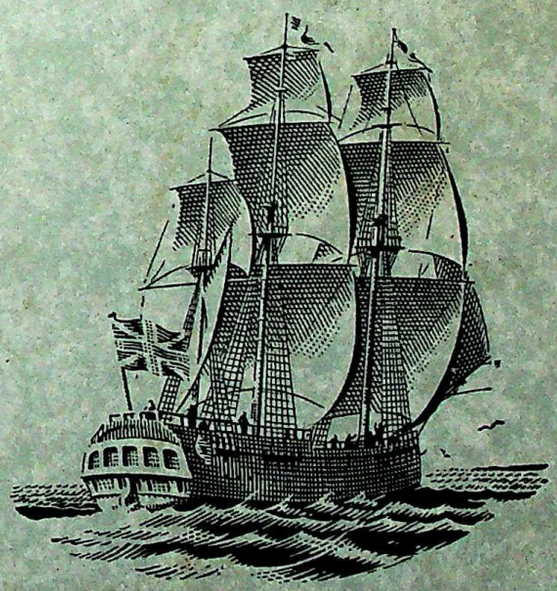

ENDEAVOUR

VOLUME XXV NUMBER 95 MAY 1966

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Endeavour

Endeavour has been published by Imperial Chemical Industries since 1942. It presents, for scientists throughout the world, a regular review of the progress of science. While the emphasis is on British science, contributions are regularly commissioned from all parts of the world; the principal considerations are the intrinsic interest and importance of the subject and the authority of the writer. To ensure international acceptance, the journal is published in English, French, German, Italian, and Spanish.

No charge is made for *Endeavour*, and it is distributed to senior scientists, scientific institutions, and libraries throughout the world. Within these limits, the Editor is always glad to consider the addition of names to the mailing list.

The drawing on the cover is of the bark *Endeavour*, which, commanded by Captain James Cook and carrying a number of scientific workers, was sent out by the British Admiralty in August 1768, following a Memorial by the Royal Society to King George III, to chart the South Pacific Ocean and observe the transit of Venus.

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ENDEAVOUR

VOLUME XXV MAY 1966

A review of the progress of science, published in five languages

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Communications should be addressed to the Editor, Endeavour, South Block, Thames House, Millbank, London S.W.1 Telephone: Tate Gallery 2181

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Scientific immigrants in the United States

Traditionally, science is an international pursuit based upon the free exchange of men and ideas, and in the past there were indeed virtually no restrictions. In 1813, for example, Davy and Faraday were received in a friendly fashion in Paris by French scientists despite the fact that their two nations were at war. Such liberal ideas now belong to the past, and although international co-operation in science is freer than in most human activities, the movement of scientists from one country to another can be a matter for concern rather than satisfaction. This is, of course, a reflection of the changed role of science in the world. From the harmless pursuit of scholars, it has become the mainspring of technological progress; scientific manpower must be conserved as jealously as all other vital national resources.

For a considerable time there has been mounting disquiet about the extent to which scientists of many countries are emigrating to the United States; this was discussed in ENDEAVOUR (**22**, 106, 1963) three years ago. A recent report[1] published by the Institute of International Education gives a detailed survey of how the situation has since developed. In general, the report indicates no sign of a break in the existing trend. Ten years ago there were 34 000 foreign students in the United States; last year there were over 80 000, and it is expected that the number will rise to 100 000 by 1970. Not only are more students going there but they are staying longer; as a diminishing number of students—now only 28 per cent—are self-supporting, the cost to the United States is very substantial.

Although few institutions of higher education have no foreign students, half of them are concentrated in only 42 institutions, mostly in California and New York. The demand for education in engineering (20 per cent of all students) has stayed surprisingly steady for many years, but the demand for places in science is slowly increasing: it is now 18 per cent of the total, compared with 12 per cent five years ago.

Even more striking is the increase in the number of foreign postgraduate workers in the United States; the total is now about 9000, representing a tenfold increase over the same period. The proportion of scientists is increasing, and now amounts to some 40 per cent of the whole, but there has been a marked decline in the humanities and medicine. The biggest single source of these postgraduate immigrants was the United Kingdom (1166, 13 per cent), followed by Japan (1108, 12 per cent), India (1002, 11 per cent), and the Federal Republic of Germany (600, 6·7 per cent).

So far as Europe is concerned, it appears at first sight that the number of postgraduate workers from the United Kingdom is disproportionately large, but the picture becomes clearer if the numbers are related to the populations of the countries involved. On this basis, Switzerland (28 per million of population) is the largest contributor to what is commonly called the brain drain, though the total number involved was only 164. Then follow, in order, the United Kingdom (22 per million), Sweden (14), Holland and Germany (11), France (7), and Italy (5). Although these figures relate to scholars of all disciplines, it is reasonable to suppose that, in the European context, they are proportionately true for science, which accounts for nearly half the total. Not all these immigrants stay permanently in the United States, for many leave after a year or two's experience; nevertheless, each wave leaves a substantial residue behind.

There seems no prospect that the United States will in the near future seek fewer postgraduate scientists from abroad; if anything, the demand is likely to increase. The American economy remains strong—a situation to which the intensive exploitation of scientific discovery has itself made a powerful contribution—and there seems no immediate likelihood of economic recession diminishing the demand. The recently published Westheimer Report[2], for example, calls for substantially increased expenditure on chemical research over the next few years, with special emphasis on support for research projects by younger men. If these recommendations are accepted, it must be assumed that over the next few years this major field of science will offer even greater opportunities to young postgraduate workers than it does at present.

What of traffic in the reverse direction? Increasingly, American scholars recognize the value of a period abroad. Last year 18 000 students and nearly 4000 postgraduates were working outside their own country, a substantial increase over the previous year; for more than half of them, the principal magnet was Europe. For the United States, a major benefit from her policy of encouraging scientific immigration is obviously the addition of exceptionally highly trained men to her total pool of technical manpower. But there is more to it than this: the immigrants bring with them not only scientific knowledge but an outlook distinctively different from that of their hosts. The importance of this aspect is being increasingly recognized in the United States, and it is significant that the foreword to the latest edition of 'Open Doors' states that 'the need for Americans with experience and insight into other cultures is steadily growing'. If the United States fully recognize their own need for broader experience, then the situation might change quite dramatically; the present disquiet arises not from the existence of a transatlantic science traffic but from its lack of balance.

Meanwhile, European scientists themselves might well take fuller advantage of the opportunities for foreign experience on their own side of the Atlantic, as they commonly did in pre-war days. A recent report[3] by the Organization for Economic Co-operation and Development stresses this point. The 'various means of international exchange, important for the health of international research, should be particularly easy and effective between the European countries'. The fashion for American experience, and the relative ease of getting it, has tended to obscure the fact that during the last decade European science has developed enormously since its decline during the war. It is probably now true that, outside certain specialized fields, there are few North American laboratories without comparable counterparts in Europe. In many instances the broadening of the mind, the learning of new techniques, and the other undoubted advantages of working abroad, are at least as satisfactorily attainable in Europe as elsewhere, and there is the additional possibility of attaining fluency in a foreign language. Stipends and the standard of living are generally less than in the United States, but should this be the only consideration? It was certainly not in those early days when science truly knew no frontiers of race or language.

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The Uncertainty Principle and short-lived atomic and subatomic states

Sir Harrie Massey

One of the practical results of Heisenberg's Uncertainty Principle is that the lines of absorption and emission spectra must have a finite width. This article describes the application of the Principle to optical and impact spectra of atoms, ions, and nuclear particles, and shows how it can be used to detect and measure the lifetimes of 'resonance particles' that exist for only 10^{-23} sec.

One of the most far-reaching consequences of quantum mechanics is embodied in Heisenberg's Uncertainty Principle, which is usually described in terms of the measurement of the position and momentum of a particle. Suppose the particle is moving in a straight line. Then, according to the Uncertainty Principle, it is intrinsically impossible to know accurately both the momentum and position of the particle at the same time. Because the particle must be considered also in terms of waves, an uncertainty Δp in the momentum is associated with an uncertainty Δx in the position of the particle, so that

$$\Delta p \Delta x \simeq h/2\pi,$$

where h is Planck's constant. (This has the dimensions of action, or of angular momentum.) No matter how refined the measuring equipment may be, any increase in accuracy in the determination of momentum must involve a decreased precision in the knowledge of the position of the particle.

This particular uncertainty relation is only one of many that involve what are referred to as conjugate physical quantities. For the purposes of this article, the most important two such quantities are the energy of a system and the time during which this is measured.

Once again, the uncertainties ΔE, Δt respectively, in the knowledge of these quantities, are related by

$$\Delta E \Delta t \simeq h/2\pi.$$

Thus if a time τ only is available for measuring the energy of a system, then there must always be an intrinsic uncertainty, $h/2\pi\tau$, in the measured energy. No improvement in the design of the measuring instrument can remove this uncertainty.

It would seem at first sight that the existence of these uncertainty limitations must obscure the discovery of relationships in the physical world, making it more difficult to determine the detailed microscopic structure of matter. In actual fact, the energy-time uncertainty relation makes it possible to extend the scope of physical investigations, particularly into the properties of very ephemeral atomic and subatomic systems.

As we have seen, the energy E of a system in a state with a finite lifetime τ will be uncertain by an amount $h/2\pi\tau$. It is a further consequence of quantum mechanics that the energy E is associated with a frequency $\nu = E/h$, and it is well known that the measurement of frequency by the use of resonance methods, for example in radio, is one of the most accurate in physics. If we can devise some such method for determining the energy of the state, it follows that the frequency at which the resonance occurs will not be sharp, but will extend over a range of energy $h/2\pi\tau$, that is, over a frequency range of $1/2\pi\tau$. By measuring the shape of the resonance response as a function of frequency or of energy, we can determine the lifetime of the state reasonably well. If we measure τ in seconds, we find that the energy width of an unstable state is given by

$$\text{Energy in eV} = \frac{6{\cdot}6 \times 10^{-16}}{\tau} \qquad \ldots(1)$$

The applications to atomic, nuclear, and high-energy particle physics that we shall now discuss span an enormous range of both time and energy (from 10^{-8} to 10^{-23} sec and from 10^{-7} to 10^{8} eV), but they all involve essentially the same principles.

Short-lived atomic states

It is best, in considering atomic states, to start with the hydrogen atom, as it contains only one electron. The pattern of the possible energies that an electron may possess when it is in the field of a proton depends on whether the electron is in a bound or an unbound state. According to quantum mechanics, the possible energies that an electron may possess when bound in a hydrogen atom are given by

$$E_n = -\frac{2\pi^2 m e^4}{n^2 h^2}$$

(where $n = 1, 2, \ldots$, and e and m are respectively the charge and the mass of an electron). The zero level of energy is that possessed by the electron when it is at an infinite distance from the atom. Thus in the nth state, the energy required to remove the electron completely from the atom is $-E_n$. The most firmly bound state, the ground state as it is called, is the one for which $n = 1$. In addition to these bound states of negative energy, an electron may possess positive energies of any value while moving in the field of the proton. These unbound states form a continuum, so that the full energy-level diagram is as shown in figure 1. For an isolated hydrogen atom, the ground state of an electron is the only state which is completely stable. An electron in an upper, excited state will eventually drop to the ground state, emitting the difference in energy in the form of radiation.

The mean lifetime of an excited state before it emits radiation is of the order of 10^{-8} sec—there are some exceptions that need not concern us here. It follows from the Uncertainty Principle that, because of this finite lifetime, the energy of an excited state will be uncertain by an amount of the order of 10^{-7} eV. This means that

Sir Harrie Massey, *B.A., M.Sc., Ph.D., F.R.S.*
Was born in 1908 and was educated at the University High School, Melbourne, and Melbourne University. After graduation he undertook research work in atomic physics at the Cavendish Laboratory, Cambridge. In 1933 he was appointed head of the department of mathematical physics at Queen's University, Belfast, and in 1938 became Goldsmid professor of mathematics at University College, London. He held this chair until 1950, when he became Quain professor and head of the department of physics at the same college. He is the chairman of the Council for Scientific Policy, and chairman of the British National Committee for Space Research.

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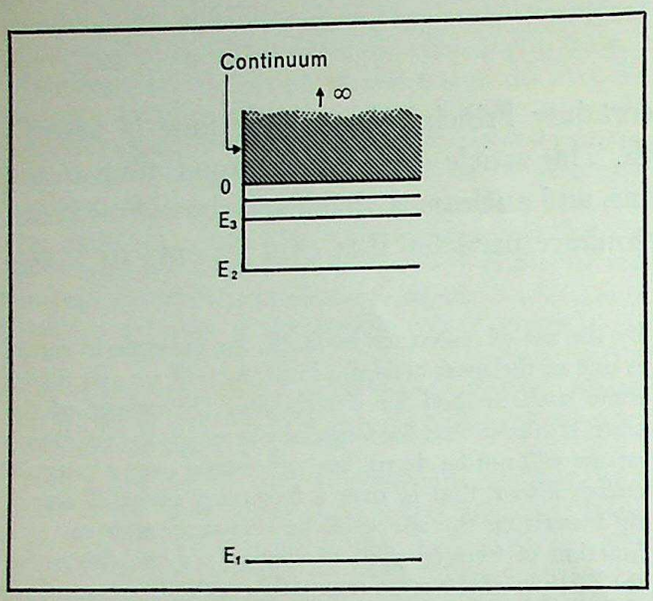

Figure 1 Allowed energy levels for the hydrogen atom.

the spectral lines emitted by the atom must have a 'natural' line width of at least this size. It is in fact only a very small width, corresponding to a frequency spread of the order of 10^{-7} of the mean frequency, and is usually obscured by other broadening effects. There are states that have shorter lifetimes, and thus produce wider lines: for these, we must turn to atoms or ions which possess more than one electron.

Absorption of radiation by the atom is possible if the frequency of the radiation is such that

$$h\nu = E_n - E_1,$$

where E_1 is the energy of the ground state and E_n of an allowed excited state which could either be bound or lie in the continuum. The absorption spectrum of atomic hydrogen will therefore have the form shown in figure 2. In this, lines arise from transitions to single excited states of negative energy, and the continuous spectrum from transitions to positive-energy states.

A rather similar type of spectrum is obtained if the atoms acquire energy from electron impact instead of from light absorption. The energy-loss spectrum—the absorption spectrum—of a beam of electrons, all of the same initial kinetic energy, passing through a gas of atomic hydrogen is similar in structure to figure 2, but the relative intensities of the lines and the continuum may be somewhat different, and will depend on the initial energy of the electrons. It is important to note that the continuum in figure 2 exhibits no structure, but only a smooth decrease of intensity as the frequency increases.

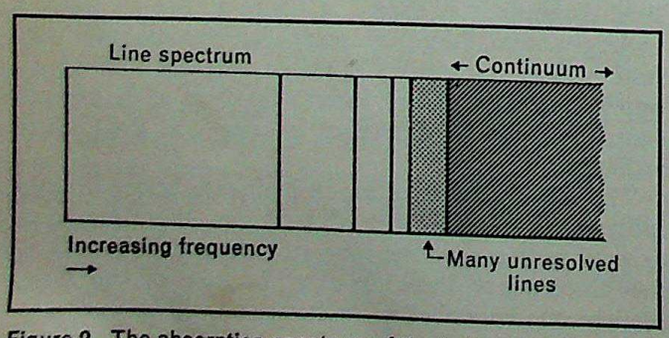

Figure 2 The absorption spectrum of the hydrogen atom.

Complex atoms and auto-ionizing states

Let us now consider the possible energy states of the helium atom, containing two electrons. As a rough approximation, we can regard the interaction between the two electrons as affecting only the detail, and not the general character, of the allowed energy-levels. This being so, we can regard each electron as moving in an effective electric field rather like that due to the proton in the hydrogen atom. We can now build up the states of the atom by adding the separate contributions from each of the electrons.

First of all, we have a set of states which are obtained if one electron remains fixed in its ground state, while the other occupies successively a similar set of states to that of the single electron in the hydrogen atom.[1] The allowed atomic energy levels will then be E_1+E_1, E_1+E_2, E_1+E_3, . . ., merging eventually with a continuum. The states of this continuum will be ones in which one electron is free of the atom while the other remains bound in the lowest state. These levels, above the

[1] More properly, we should regard the electrons as continually interchanging, but this has no effect on the argument—at any time one of the electrons is in the ground level, the other in the excited level.

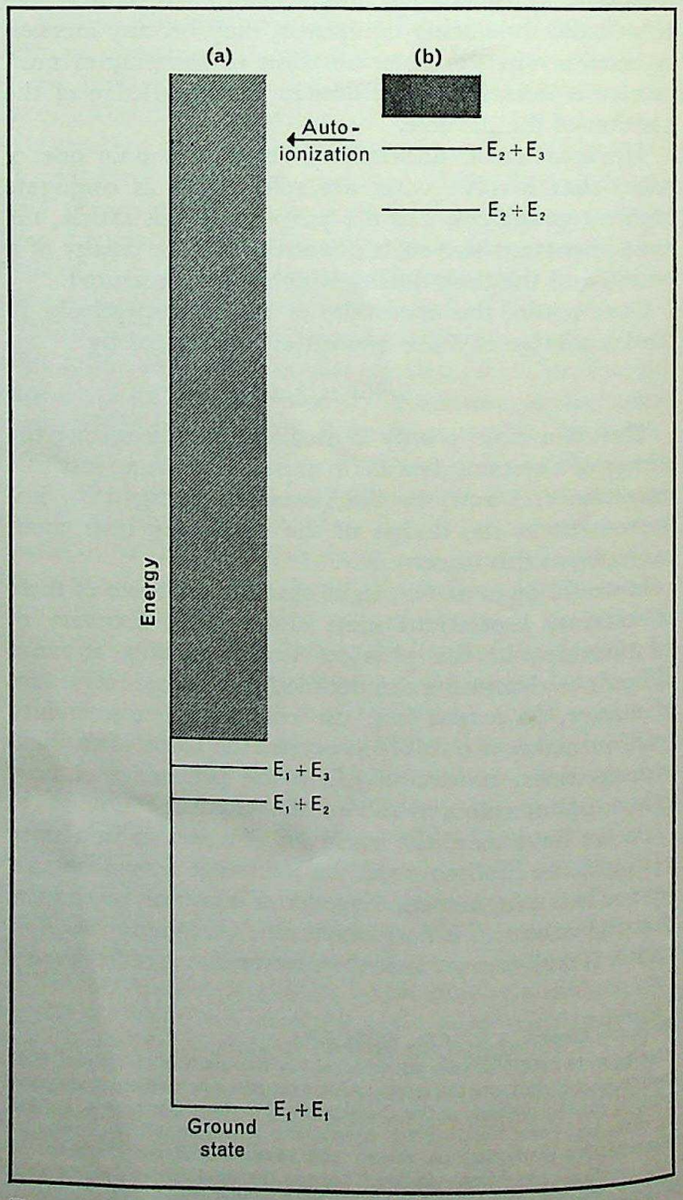

Figure 3 Schematic energy-level diagram for the helium atom. (a) Singly excited states; (b) Doubly excited states.

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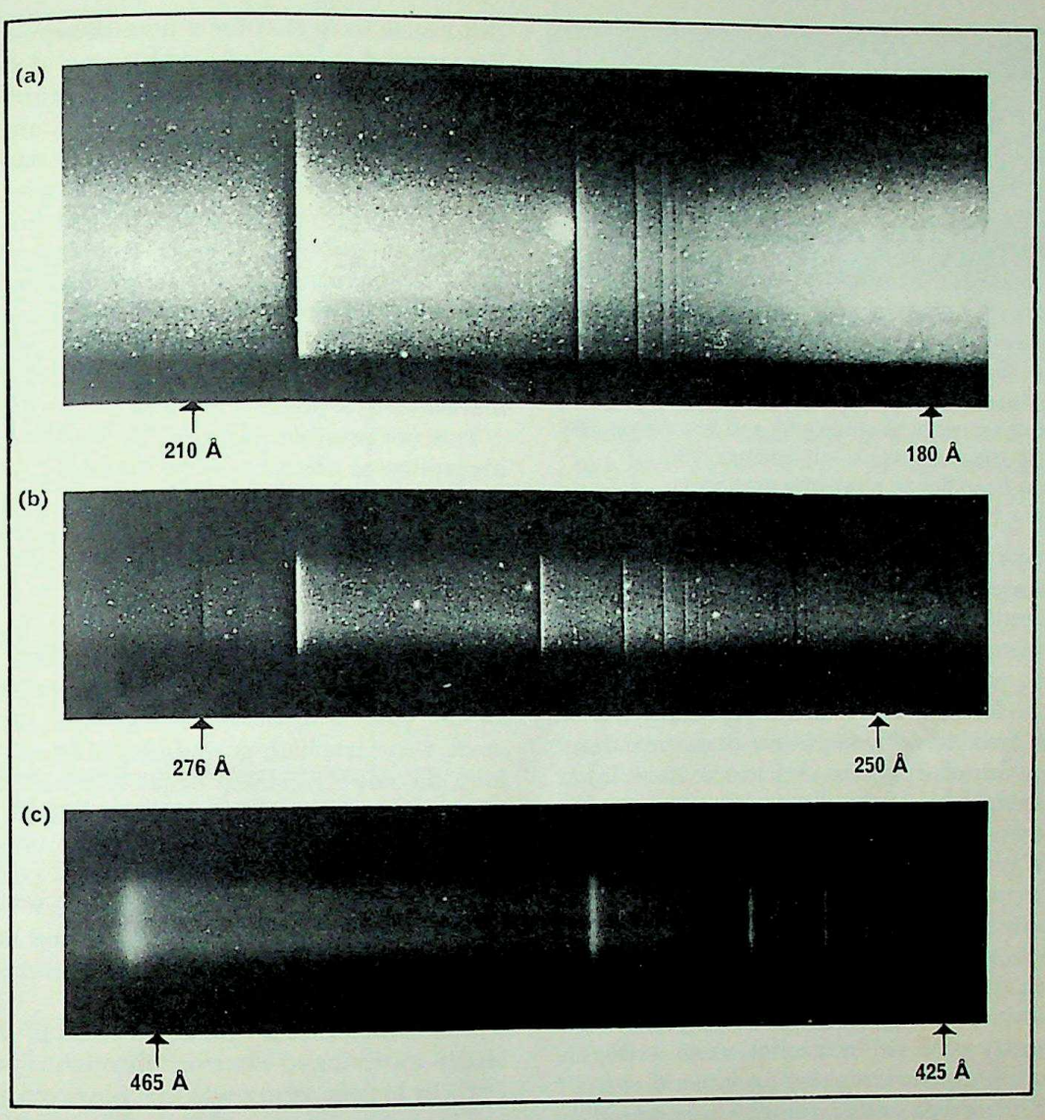

Figure 4 Absorption spectra of rare gases in the far ultraviolet observed by Madden and Codling. (a) Helium. (b) Neon. (c) Argon.

ground level, are known as singly excited states, and give rise to the scheme shown in figure 3(a).

So far, the pattern is similar to that for hydrogen: but we must now include a further possibility which does not arise at all in atoms or ions with only one electron—both electrons may be in excited states. The lowest of the doubly excited states will have a total energy close to E_2+E_2. However, in general, the energy of the doubly excited atomic states is always greater than the combined energy of the system in which one electron is in its ground state and the other is free of the atom at infinity. The situation is as shown in figure 3(b). Under these circumstances, the existence of an interaction between the electrons ensures that, before very long, one electron in a doubly excited state will make a transition to the ground state. The energy released is taken up by the second electron and is sufficient to remove that electron from the atom altogether.

This transition is unlike those between singly excited states, as no outside interaction is necessary. All that happens is that the total energy is redistributed between the two electrons. This phenomenon is known as auto-ionization and causes the lifetime of a doubly excited state to be normally much shorter (about 10^{-13} to 10^{-14} sec) than that of a singly excited state.

The shortness of these times naturally prompts the question as to whether a situation as ephemeral as this can really be regarded as an approximately 'stationary' state at all. In fact, however, this interval is long enough for an electron in a bound orbit to make about 100 revolutions, and is quite sufficient for identification of the orbit.

In terms of the energy-time Uncertainty Principle, the short lifetime means a much greater blurring of the energy of a doubly excited state. Thus on substitution in equation (1), we find that the energy spread corresponding to lifetimes between 10^{-13} and 10^{-14} sec is between 0·007 and 0·07 eV. The observation of energy spreads of this magnitude is within reach of a number of experimental techniques, and the experimental study of auto-ionizing states is now being vigorously pursued.

What effects are we to look for? Let us first of all consider the absorption spectrum of helium atoms. We must now allow for the possibility of excitation that produces a transition from the ground state to a doubly excited state. The frequency of radiation which can cause this is exactly that required to produce a transition to a singly excited continuum state, as is apparent from figure 3. We might expect then that, superposed on the

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Figure 5 Energy-loss spectrum of electrons scattered from helium atoms as observed by Whiddington and Priestley in 1934. The line due to double excitation is indicated as $(2P)^2$, and O denotes the lines due to elastically scattered electrons.

continuous absorption, there will be lines due to excitation of doubly excited states. The very short lifetimes of these states means that the lines will be much broader than those that appear at frequencies below the first ionization limit. In fact, the width of the lines due to auto-ionization is 10^5 to 10^6 times larger than the natural radiative line-width of singly excited states; these latter widths are increased by other effects, but even so, the lines due to auto-ionization are very much wider. In short, we would expect rather broad 'bumps' to be superposed on the continuous absorption.

The situation is a little more complex than this because of the wave aspect of the phenomenon. Absorption may occur at certain frequencies beyond the ionization limit in two alternative ways—by direct transition to a singly excited continuum state or by excitation to a doubly excited state which auto-ionizes after an interval of 10^{-14} to 10^{-13} sec. The probability amplitudes corresponding to each of these effects will interfere, because they are associated with the same frequency. This may lead to either enhancement or reduction of absorption intensity, depending on the relative phase of the two amplitudes. In some cases, then, we can expect that there will be decreased absorption, a rather remarkable effect.

Figure 4 reproduces some absorption spectra for helium, neon, and argon, obtained by R. P. Madden and K. Codling [1], that show both enhancement and reduction of the absorption intensity. For the first two atoms, broad absorption lines due to excitation of auto-ionizing states are clearly seen. In argon, on the other hand, such excitations are manifest in the presence of broad lines of increased transparency, rather like emission lines.

As long ago as 1934, R. Whiddington and H. Priestley [2] observed a broad peak in the energy-loss spectrum of electrons that had passed through helium gas. This was interpreted correctly as being due to double excitation. Figure 5 shows the electron energy-loss spectrum exhibiting the peak in question. Because research in electron energy-loss spectra demanded that the electron energy be defined to better than 0·1 eV before and after impact, there was little further progress till recently, but much work is now being done in this field.

Unstable states of negative ions

The energy-level system for a negative ion—a neutral atom plus an additional electron—shows some major differences from that for a neutral atom or positive ion. The ground state will be stable only if its energy is less than that of the ground state of the neutral atom, that is, if energy must be supplied to detach an electron. Thus H^-, for example, has a stable ground state, He^- has not. All negative ions have very few, if any, singly excited states that are stable towards detachment. However, all possess doubly excited states with a lifetime in terms of autodetachment of about 10^{-13} to 10^{-14} sec. Autodetachment is the equivalent of auto-ionization for these cases—the only difference is that the radiationless transitions lead to a neutral atom and a free electron, instead of to a positive ion and a free electron.

It is not possible to study the autodetaching states by absorption or electron energy-loss spectra because of the difficulty of obtaining a sufficient concentration of negative ions. An alternative method is to use the process that is the reverse of autodetachment. This is the reaction

$$He + e \rightarrow He^{-\prime\prime}$$

where $He^{-\prime\prime}$ denotes a doubly excited state of He^-. When an electron with energy of exactly the right value for this process to occur collides with a neutral helium atom, there is a high probability of its being captured to form the doubly excited negative ion. After an interval of about 10^{-13} to 10^{-14} sec, this will break up to yield an electron with the same energy, but moving in a different direction. Thus the existence of the state provides an additional scattering process that may be very strong. Its formation is a resonance process and the width of the line involved is determined by the lifetime of the doubly excited state.

The existence of a resonance effect of this kind in the elastic scattering of electrons through a particular angle (72°) by helium atoms was first observed by G. J. Schulz [3] in 1963. It was confirmed a little later by J. A. Simpson and S. R. Mielczarek [4], who observed the

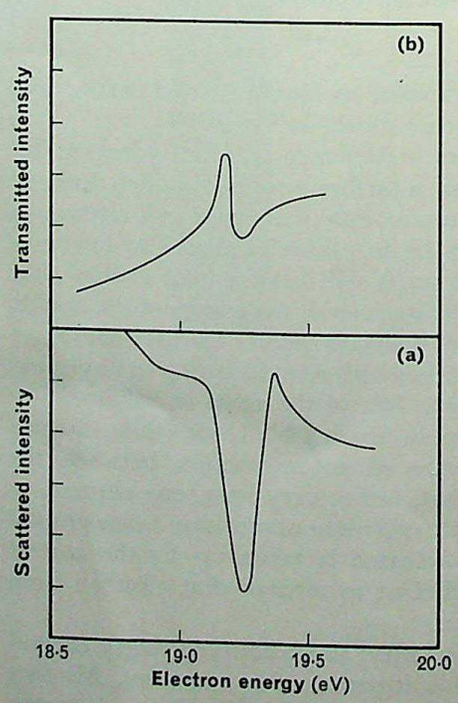

Figure 6 Observed resonance phenomenon in elastic scattering of electrons by helium atoms. (a) Variation of scattered intensity at 72° with electron energy. (b) Variation with electron-energy of the intensity of an electron beam after transmission through helium gas.

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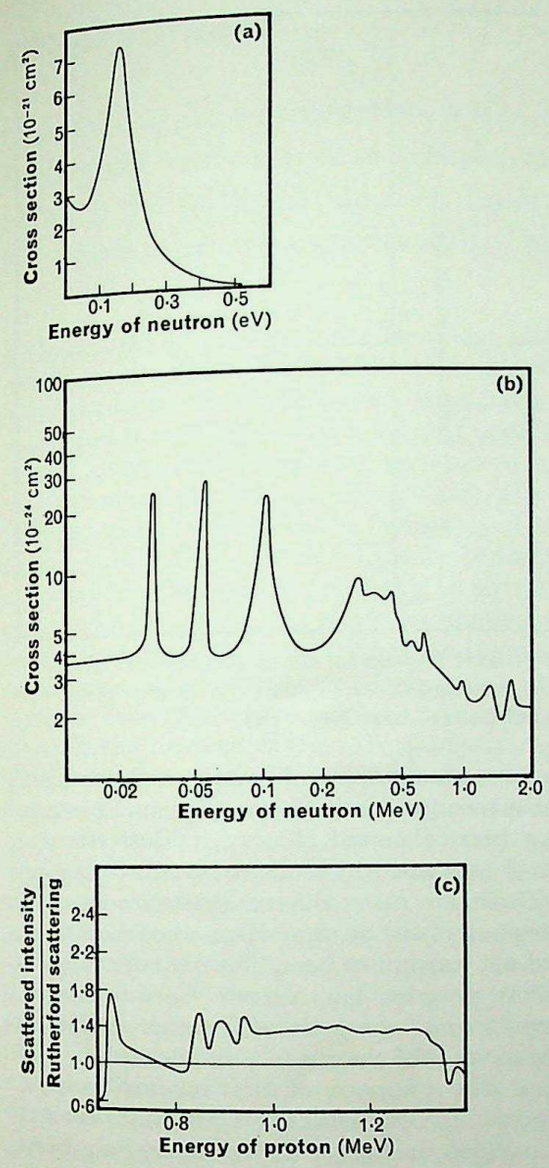

Figure 7 Resonance phenomena in collisions of nucleons with nuclei. (a) Total cross section of cadmium for slow neutrons as a function of neutron energy. (b) Total cross section of fluorine for neutrons with energies in the range 0·01–2·0 MeV. (c) Variation with proton energy of the intensity of electron scattering of protons through a large angle by fluorine nuclei. The intensity is given as a ratio to that for scattering by a point charge equal to that of the nucleus (Rutherford scattering).

variation with electron energy of the intensity of an electron beam after transmission through helium gas. Figure 6 illustrates their results. In these cases, the resonance, through interference, reduces the scattering. This is an effect similar to that which produces the bright absorption lines in figure 4(c). Similar resonances have recently been observed in other rare gases. Once again, the phenomena would have been observed much sooner had it been possible to obtain a sufficiently fine resolution of the energy of the incident and scattered electron beams.

Unstable states of nuclei

Resonance effects in nuclear collisions with nuclei were first observed by J. Chadwick, J. E. R. Constable, and E. C. Pollard in 1931 [5]. They measured the yield of protons from the disintegration of light nuclei by α-particle impact as a function of the energy of the α-particles. It was found that the yield function showed a number of broad peaks. Although the origin of these peaks was not fully understood at first, they are now known to arise through resonance capture of α-particles to form an unstable nuclear complex which, after about 10^{-19} sec, breaks up to produce a proton and a residual nucleus.

A very great variety of resonance effects have since been observed in nuclear collision phenomena. Some examples are shown in figure 7. Figure 7(a) shows the observed total absorption cross section[1] of cadmium towards slow neutrons [6]. The resonance peak at a neutron energy of 0·178 eV is clearly prominent. The width of the resonance is about 0·1 eV, corresponding to a lifetime of 7×10^{-15} sec for the complex formed by resonance capture of the neutron. This is only about 10 times shorter than the lifetimes of the autoionizing atomic complexes that are discussed above. At first sight this seems surprising, because a nuclear complex is about 10^4 times smaller in diameter and we might expect its lifetime to be correspondingly smaller. However, in a close collision with a nucleus, a neutron experiences much more powerful forces than does an electron on impact with an atom. This means that the initial energy of the neutron is soon distributed among a large number of nucleons (protons and neutrons): there are 113 in a cadmium nucleus. A relatively long time elapses before sufficient energy is re-concentrated in any one nucleon for it to leave the system. In fact, this time is so long that it is possible for the complex to be stabilized by radiation of the surplus energy in the form of γ-rays. Atomic auto-ionizing complexes are relatively so short-lived that there is little chance for radiation to occur. In contrast, if there were no probability of radiation, the complex formed by resonant capture of a neutron by a cadmium nucleus would have a mean life 100 times longer. This follows from the observed result that it is a hundred times more probable that a neutron, after forming a complex by collision with a cadmium nucleus at the resonance energy, will remain captured through emission of the surplus energy as radiation than that it will be re-emitted with its initial energy.

For collisions involving light nuclei, there is a smaller number of nucleons to share the excess energy. The lifetime of a resonant complex is therefore so much shorter that the chance of radiation is small relative to that of some process involving particle emission or elastic scattering. This leads to much greater widths of the resonances, as may be seen in figures 7(b) and 7(c), for impacts of neutrons and protons with fluorine nuclei.

Unstable states of nucleons and mesons

One of the most remarkable applications of the resonance technique for detecting excited states of systems and determining their lifetimes has been to the discovery of the so-called resonance particles. These are short-lived excited states of nucleons and of mesons.

Neutrons and protons, the structural units of nuclei, are held together by forces transmitted largely through the emission and absorption of π-mesons or pions, just as the electrons and positively charged nuclei in atoms are held together by electrical forces transmitted through

[1] The absorption cross section Q_a is the effective area of absorbing target that a nucleus presents to a neutron.

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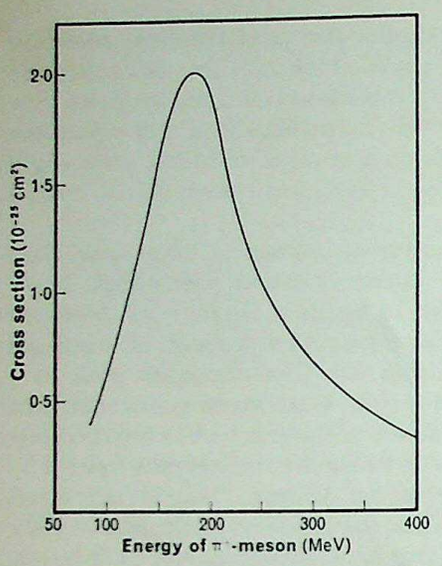

Figure 8 Total cross section for scattering of π^+-mesons by protons as a function of meson energy.

emission and absorption of electromagnetic radiation or photons. Pions differ from photons in possessing a finite rest mass and three charge states. Thus there are positive and negative pions of mass 273 times that, m, of an electron and charge, $+e$ and $-e$, respectively, and neutral pions of mass $264m$. These are denoted by π^+, π^-, and π^0 respectively.

Figure 8 shows the observed variation with energy of the cross section for scattering of π^+-mesons by protons [9]. The typical resonance peak is prominent, but now the width is measured in terms of MeV instead of eV, showing that we are dealing with an unstable state with a lifetime as short as $0{\cdot}75 \times 10^{-23}$ sec. This is only a little longer than the time taken to traverse, at the velocity of light, the diameter of a proton, but nevertheless the resonance shows up clearly in the observations. The state concerned is a doubly charged excited state of a proton, and the scattering phenomenon is essentially similar to resonance fluorescence in the scattering of light. If N^{++} denotes the excited proton state, the scattering in the resonance region proceeds through the two successive reactions

$$\pi^+ + p \rightarrow N^{++},$$
$$N^{++} \rightarrow p + \pi^+,$$

where p denotes the proton.

Another way in which the transitory formation of N^{++} is observable is through the reaction

$$\pi^+ + p \rightarrow \pi^+ + \pi^0 + p.$$

There is strong evidence that it proceeds through the two stages

$$\pi^+ + p \rightarrow \pi^0 + N^{++},$$
$$N^{++} \rightarrow p + \pi^+.$$

Thus it is found that there is a strong correlation between the direction of emission of the proton and that of the π^+ meson. This would be expected only if these two particles result from the breaking up of a single system, for in that case the correlation is required to conserve energy and momentum. If the process proceeded directly so as to produce three particles, little correlation would be expected.

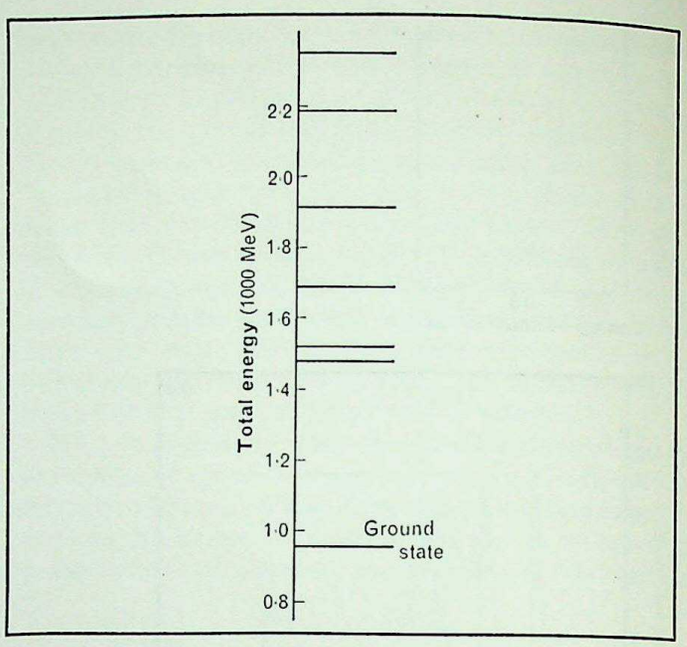

Figure 9 Energy-level diagram for states of a nucleon which may be reached through pion absorption. The energy given includes the nucleon rest mass (940 MeV).

From extensive observations of reactions of this kind, a remarkable spectrum of excited states for nucleons and for pions has been observed. Figure 9 illustrates the excited states of nucleons which may be reached by pion absorption. There are many others which are reached through absorption of one or more K-mesons, the nature of which need not concern us here. The data are so comprehensive that progress has already been made in discerning regularities—the position is rather similar to that at the beginning of the century in the ordering of optical spectra. The symmetry of these schemes made it possible to predict the existence of certain other excited states of the nucleon, including the relatively long-lived Ω^- particle (mean life $0{\cdot}7 \times 10^{-10}$ sec). These states have since been observed in experiments, which suggests that the proposed ordering is on the right lines. However, although the results fit the empirical formulae, there is no sign yet in high-energy physics of an understanding equivalent to that given by Bohr and Schrödinger to atomic physics.

Acknowledgments

I am grateful to Dr Madden for furnishing me with the photograph reproduced in figure 4 and to the Royal Society and Professor R. Whiddington, F.R.S., for permission to reproduce the spectrum shown in figure 5.

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Cytoplasmic continuities during spore formation in flowering plants

J. Heslop-Harrison

One stage in the reproductive cycle of flowering plants is meiosis, which eventually results in spores. During the early stages of meiosis, massive strands produce a complete cytoplasmic continuity between the participating cells. Later, the mother cells and the spores they produce are isolated from each other by a special wall. This article discusses some of the implications of these events.

Although the life cycle of the flowering plant is sufficiently like that of the higher animal for the principles of Mendelian heredity to be equally applicable to both, it differs fundamentally in that it is based upon an alternation of generations. The plant we observe is diploid—that is to say, it has two chromosome sets in its cells—and its reproductive process is the formation of spores by a reducing, or meiotic, nuclear division; hence it is termed a sporophyte. The spores germinate to give microscopic plants with the haploid or single-set number of chromosomes; these form gametes, also with the haploid chromosome number, and hence are known as gametophytes. Gametic fusion restores the diploid number in the zygote, which is the first cell of the new sporophyte generation. This type of life cycle is seen much more conspicuously expressed in the ferns, where the gametophyte is free-living. In flowering plants, the gametophyte generation is greatly reduced in duration and cell number. The microspore undergoes only two cell divisions in the formation of the gametophyte and the male gametes carried in the pollen grain and pollen tube. A total of seven nuclear divisions is involved in the production of the egg in the female gametophyte, or embryo sac, contained in the ovule. Moreover, the gametophytes are nutritionally dependent upon the parent sporophyte, and the female gametophyte, indeed, has no independent life outside the sporophyte.

Since the outcome of the reduction of the gametophyte generation in the course of evolution has been to establish a life cycle virtually identical with that of the higher animals, it is easy to overlook its true complexity, and botanists who insist on emphasizing the dissimilarities run some risk of being accused of pedantry. Yet, concealed though it may be, the alternation of generations in the flowering plant life cycle has some unusual physiological and genetical consequences. The reduction division in the animal produces gamete nuclei that are genetically heterogeneous because of the gene segregation and recombination occurring in the meiotic prophase, the first stage of meiosis. The gamete cells themselves, however, form a uniform population, both structurally and in terms of behaviour, because their properties are determined in the main by the parent and not by the nuclei they carry. The haploid genome—the chromosome complement—is therefore not put to a functional test. The situation is quite different in the flowering plant, since there are somatic functions in the gametophytes that are directed exclusively by the haploid genome. An example is seen in those plants that have a gametophytic control of an incompatibility mechanism. Because pollen grains carrying particular genes contain substances which react in an inhibitory manner with others present in the stigmas of plants carrying the identical genes, certain pollinations—including self-pollination—are ineffective, so that outbreeding is enforced. The synthesis of incompatibility substances in the pollen grains is governed by genes acting in the haploid nuclei, and because the parent is always heterozygous, one pair of microspores in each tetrad (set of four cells) arising from a meiosis will form one type, and the other pair another.

One might surmise from this that the flowering plant will be faced in a spore sac such as the anther with a problem comparable with that presented during the intra-uterine development of a family of mammalian embryos—the need to prevent developmental interaction between individuals now about to demonstrate their genetical heterogeneity, and between them and the parent.

To date, there has been little or no investigation of this matter in flowering plants, yet there are features of microsporogenesis which do offer some pointers, in particular the sequence of changes in cytoplasmic continuity between sporocytes, and later between the microspores arising from meiosis. In large part, these changes are mediated by a special wall, formed around the sporocytes in the meiotic prophase. This article is devoted to an examination of the detailed history of this wall and to some speculation on its role.

Chemistry of the sporocyte wall

The material of the special sporocyte wall was first recognised as being chemically unique by L. Mangin [1], who named it callose. It occupies a special place among the wall substances of higher plants. Although it is never formed as widely and abundantly as cellulose, it is functionally remarkable in two respects: firstly, in the great rapidity with which tissues can form or destroy it [2], and secondly—as may be inferred from evidence mentioned in this article—in its permeability. Characteristically, it is deposited in highly homogeneous masses, and generally it is present in tissues only for short periods, acting as a seal or plug. The role of callose as a sealing agent may be seen in cells of a stem cortex adjoining the site of an injury. Here it is deposited quickly in pits in the cell walls and it thus blocks the tubes that normally connect cells, and severs the contacts with the neighbouring damaged and potentially necrotic tissue. W. Eschrich considers that a similar deposition of callose on sieve plates in the phloem occurs within seconds of injury, and has referred to it as a 'lightning' response [2, 4]. A plugging function of callose that is not a response to wounding occurs during the growth of pollen tubes through the

J. Heslop-Harrison, *M.Sc., Ph.D., D.Sc., F.L.S., M.R.I.A., F.R.S.E.*
Was born in Middlesbrough, Yorkshire, in 1920 and was educated at Chester-le-Street Secondary School and King's College, University of Durham. He was Lecturer in Agricultural Botany in the University of Durham (1946), Lecturer in Botany at the Queen's University, Belfast (1946–49), and Lecturer and then Reader in Botany in London University (1950–54). He was appointed Professor of Botany in the Queen's University of Belfast in 1954, and became Mason Professor of Botany in the University of Birmingham in 1960.

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styles of long-styled plants. While the tube is passing through the tissues of the style, the protoplast does not increase markedly in volume; instead, as it presses ahead, it progressively abandons the older sections of the tube and seals itself off from them every so often by forming a plug of callose.

It has been shown by G. Aspinall and G. Kessler [3, 5] that callose is an unbranched β-1,3-linked glucan. The deposits it forms in plant cells are remarkably pure, and it seems that there are normally no other associated wall substances. It is isotropic [5], and shows no structure electron-microscopically, whatever the method of preparation [6, 7] (figures 11–14). Callose isolated from sieve-tubes yields only very diffuse X-ray diffraction patterns; these may indicate a structure with a period of 15 Å [8]. There is thus no evidence of a microfibrillar organization, and little to indicate any marked crystalline structure; callose therefore stands in some contrast to the β-1,3-linked xylan occurring in the walls of *Caulerpa* and related algae, as this exists in double-stranded helices, 13·7 Å in diameter, aggregated in distinctive microfibrils [9].

The recognition of callose cytologically, *in vivo* or in fixed material, is facilitated by a test introduced by K. Arens [10] using aniline blue decolorized in alkaline solution at very low concentration. The dye is adsorbed and stabilized in the molecular framework of callose [5] and then fluoresces vigorously when excited in the near-ultraviolet. This method was used to obtain the fluorescence photomicrographs of figures 2–7, which show the history of the formation and disappearance of the callose special wall during the formation of pollen grains in *Lilium henryi*.

Figures 2–7 Formation and dissolution of the special callose wall in *Lilium henryi*. The photomicrographs are of anther sections excited in the near-ultraviolet after staining with aqueous aniline blue. Callose shows intense fluorescence, and starch grains in the cells of the anther wall also show some activity. (×95)

Figure 2 Pre-meiotic. The spore mother cells show no activity, nor is there any fluorescence material in the surrounding layer of nurse cells, the tapetum; the anther loculus thus appears empty.

Figure 3 Leptotene-zygotene. The callose wall is now forming around the meiocytes, and is thickest in the cell corners. There is still no activity in the tapetum.

Figure 4 Diplotene-diakinesis. The callose special wall is now complete around each meiocyte.

Figure 5 Dyad. Following the first meiotic division, a further callose wall has been formed across the equator of each meiocyte, isolating the dyad nuclei.

Figure 6 Tetrad. Meiosis is complete, and two further walls have formed to produce the tetrad.

Figure 7 Young pollen. The callose wall of the tetrad has been dispersed, and the young spores lie free in the anther loculus. The material of the pollen wall (exine) shows slight fluorescence, and plaques of the same material on the faces of the tapetal cells make this tissue visible.

The special wall during the meiotic prophase

The pollen grains of flowering plants are formed in a compartment in the anther from a mass of equal-sized cells, the pollen mother cells. Initially this tissue, the archesporium, looks like a normal meristem (figure 9). The mother cells are enclosed in cellulose walls, and their protoplasts are in communication through plasmodesmata (protoplasmic fibrils) 200–280 Å in diameter. This is the normal size for plant tissues [11]. The cross sectional area of the plasmodesmata between two mother cells accounts for perhaps 0·34 per cent of the interface, but the individual diameter of each is so small that they do not offer a free pathway for most cell components. Indeed, if, as is possible, each already accommodates an attenuated tubule of the endoplasmic reticulum, it would be unlikely that even a single globular protein molecule of, say, 70 Å diameter could move between cells.

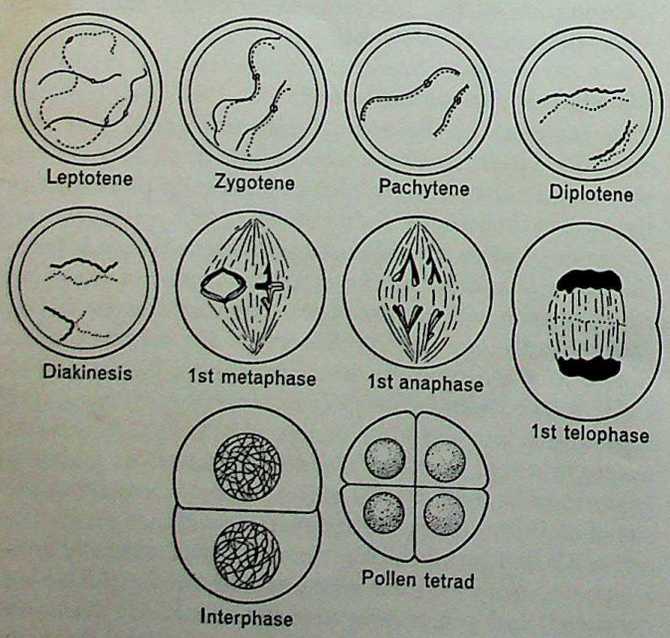

Figure 1 The stages of meiosis. (Only two chromosome pairs are shown.) There is a second metaphase, anaphase, and telophase between interphase and the pollen tetrad. (Adapted by courtesy of the publishers, Edinburgh University Press, from 'The Living Plant' by Alan Brook.)

The deposition of the callose wall begins early in the meiotic prophase, usually in late leptotene (figure 1). The first thin deposits appear in the corners of cells within the original mother cell wall, which may itself persist—with progressive gelatinization—throughout meiosis. It is well known that when the primary walls of parenchymatous cells are laid down by the deposition of microfibrillar cellulose, the dictyosomes (the Golgi bodies) of the cell are implicated; they generate vesicles which eventually discharge at the cell membrane, and evidently contain cellulose precursors [12], and it is reasonable to enquire whether the dictyosomes are involved in callose formation. They can be seen to be active at this stage, and certainly the cytoplasm of the mother cells is well populated with vesicles. W. Eschrich [7] has shown that some of these vesicles contain a material giving an electron-dense precipitate with lead acetate, and that similar precipitates can be distinguished within the newly formed callose. From this he has concluded that the vesicles contain phosphorylated callose precursors which are discharged at the cell membrane during wall synthesis. However, the electron-microscopic evidence is confused, since the cell membrane is involved in the ingestion of droplets during the meiotic prophase [13], and just how many classes of 'vesicles' are present in

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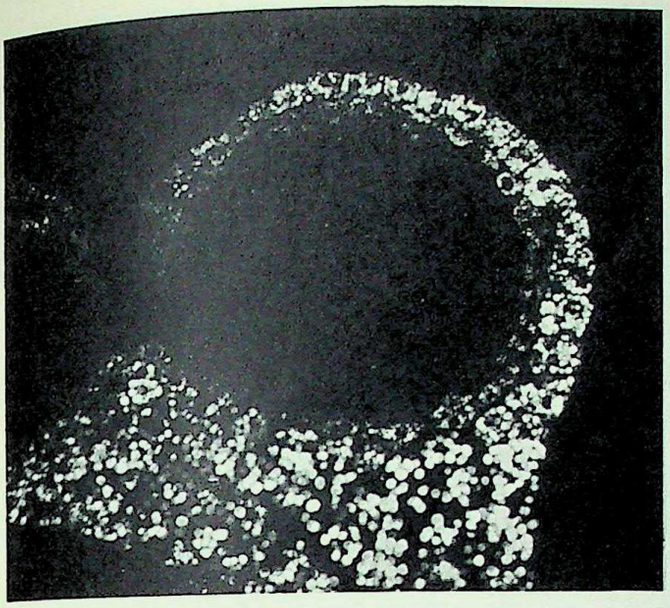

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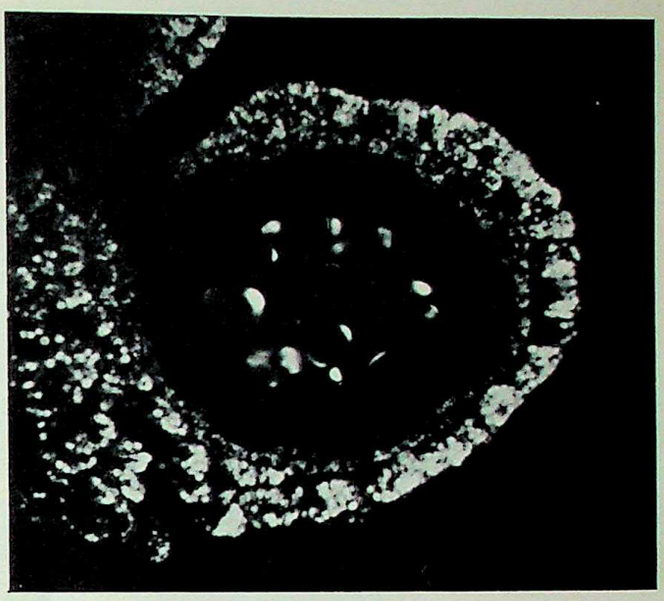

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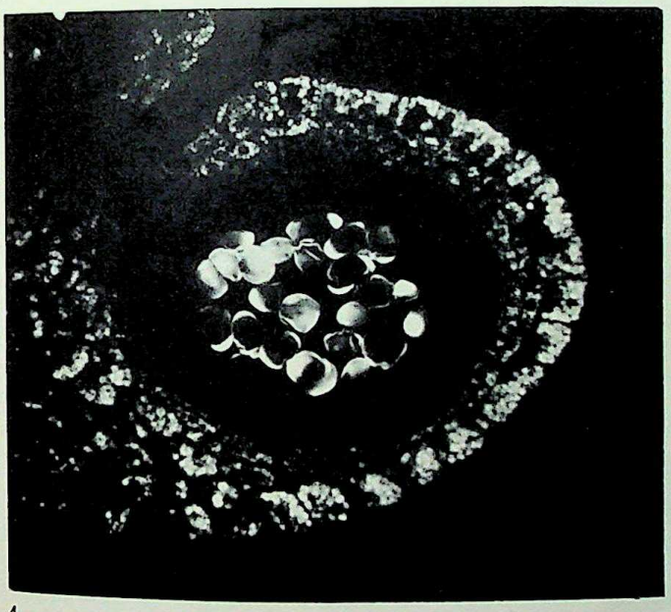

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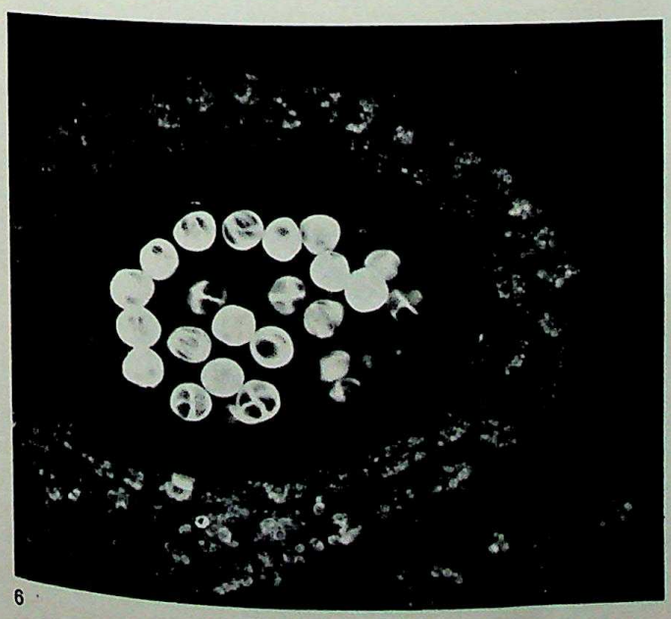

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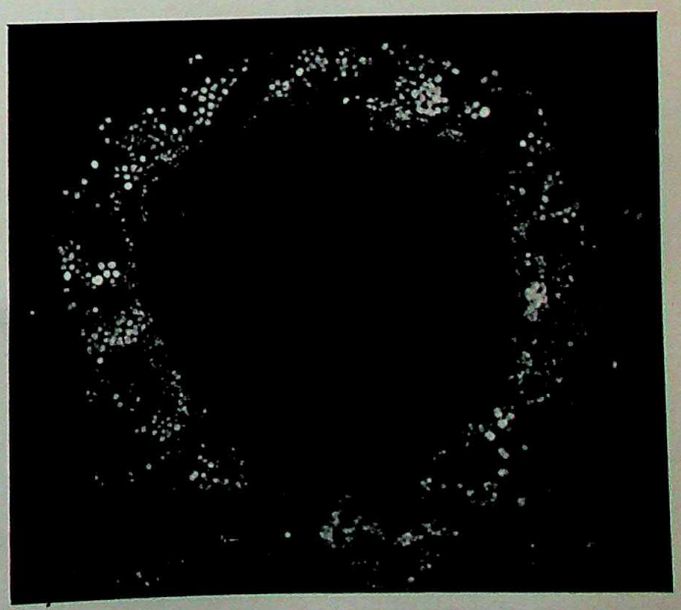

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the meiocyte cyto-plasm at this time is something still to be established.

While the new callose walls are forming around the mother cells, the cytoplasmic continuity between them is actually increasing. Massive secondary channels are defined, seemingly fewer in number than the original plasmodesmata, but very much wider—ranging, indeed, up to 1·5 μ in diameter (figures 10–13). Through the formation of these channels, cytoplasmic continuity may be established between contiguous cells over 20 per cent or more of an interface [14]. These interconnections between meiocytes—the cells that are preparing for division—were observed first by R. R. Gates [15], who noted an apparent movement of nuclear material through them, a phenomenon he termed cytomixis. The investment of the channels by continuous cell membranes can readily be demonstrated in electron micrographs (figure 11), and the continuity of membranes of the endoplasmic reticulum through its channels is frequently apparent (figure 12). Cytomixis in the sense of Gates is illustrated in figure 13.

The interconnecting channels persist until the close of the meiotic prophase; thereafter they are progressively severed (figure 14), and the meiocytes become entirely isolated within independent callose walls. In *Lilium*, the isolation is essentially complete by the end of pachytene, a mid-stage in prophase, but in some dicotyledons, such as hemp, occasional channels may remain until the end of the first division.

The tetrad wall

The separation of daughter cells after the meiotic divisions progresses according to one of two basic patterns. In most monocotyledons, a cell plate is formed after the conclusion of the first meiotic division, giving a two-cell stage (figure 5), and further plates at right angles are generated after the second division to produce the tetrad —the four-celled stage with which meiosis ends. As in a normal mitotic division in a meristem, these cell plates appear across the equator of the phragmoplast, the part of the spindle remaining between the telophase nuclei in the last stage of division. There is no deposition of cellulose primary walls, however, and the cell plates receive instead a further coating of callose. No plasmodesmata are ever formed between the daughter cells of either division, so that at the close of meiosis, each individual haploid microspore lies wholly ensheathed in callose, enclosed in the tetrad but quite isolated from its neighbours.

In many dicotyledons there is no two-cell stage, and the tetrad is formed by simultaneous cleavage after the second meiotic division. The process has been fully described in *Helleborus* by L. Waterkeyn [16]. The daughter nuclei of the second meiosis lie at the points of a tetrahedron, in two pairs linked by the residual phragmoplasts. Four secondary spindles are then formed, so that all four nuclei are linked. Cell plates are established across the equators of all six spindles, and callose is deposited centripetally across each face.

The first of the patterned walls that coats the pollen grains is formed while the tetrad is still intact [17], and not until this process is complete is there a rupture. The breakdown of the callose wall when it comes is speedy and total. It is mediated by a callase, shown by W. Eschrich [18] to be active in anther extracts of *Cucurbita* only during the precise period when dissolution of the tetrad wall is in progress. The enzymic hydrolysis of callose yields glucose and 1,3-linked oligosaccharides such as laminaribiose and laminaritriose; these products are conspicuous in the anther fluid only during the breakdown of the tetrad wall.

Figure 9 Electron micrograph of the spore mother cells of a terrestrial orchid, *Dactylorchis fuchsii*, after the final pre-meiotic mitoses. The walls (*w*) are cellulosic, and are traversed by spindle-shaped plasmodesmata (*pd*). *n*, nucleus. (× 5300, $KMnO_4$ fixation)

Figure 10 Corners of three meiocytes of *Dactylorchis fuchsii* in late leptotene. Deposition of callose (*c*) has begun inside the primary cell wall (*w*), and the plasmodesmata have been replaced by wide cytoplasmic links. (× 12 100, $KMnO_4$ fixation)

Figure 11 Single interconnection between two meiocytes of *Cannabis sativa* (hemp), showing continuity of the cell membrane. (× 38 000, $KMnO_4$ fixation)

Figure 12 Multiple channels between meiocytes of hemp at zygotene-pachytene. Continuity of profiles of the endoplasmic reticulum can be traced between the cells. (× 65 000, $KMnO_4$ fixation)

Figure 13 Movement of nuclear material (*n-n*) through a channel connecting two meiocytes of hemp. (× 23 800; OsO_4 fixation, uranyl acetate post-staining)

Figure 14 Severed inter-meiocyte channel in *Lilium henryi* at pachytene. The homogeneity of the callose wall (*c*) may be observed. On its outer surface there is a residue of the original mother cell wall; within the plasmalemma is re-forming. (× 23 800, $KMnO_4$ fixation)

Significance of the cytoplasmic connections and the callose wall

A time schedule in relation to the events of meiosis is given in figure 8 for the formation and elimination of the cytoplasmic connections and the callose wall in *Lilium*. There may be some variation in other species in the exact periods of wall formation and persistence of cytoplasmic channels, but it is likely that the basic pattern of these happenings during microsporogenesis is common to all angiosperms, and, from what evidence is available, to other higher plant groups also. It is interesting to speculate on the function of the connections and the wall.

The area of interconnection between neighbouring meiocytes increases by a factor of perhaps 60 between the pre-meiotic state and mid-prophase, and the individual

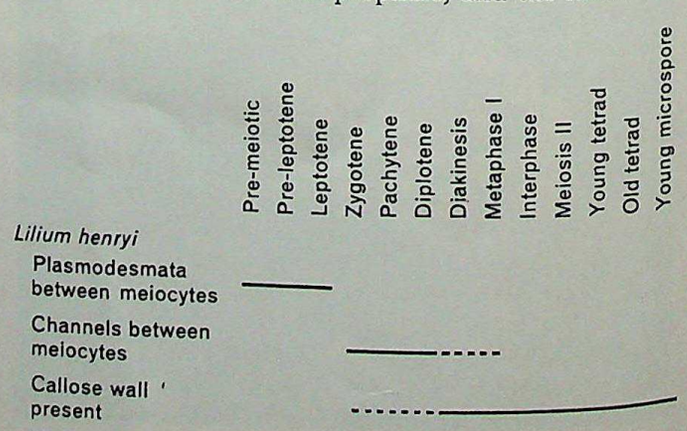

Figure 8 Timing of cytoplasmic channel and callose wall formation in relation to the meiotic divisions in *Lilium henryi*. The interrupted line indicates periods of formation or dissolution.

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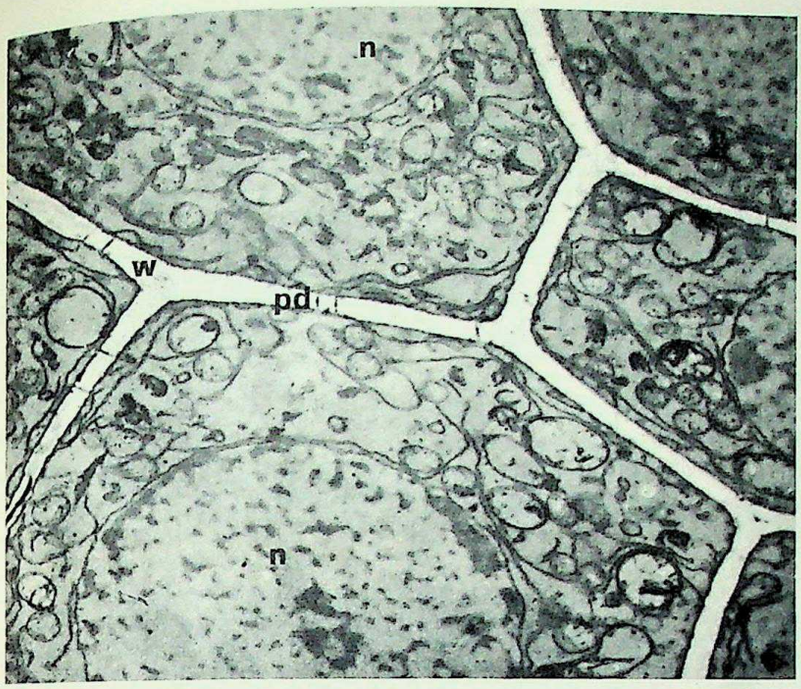

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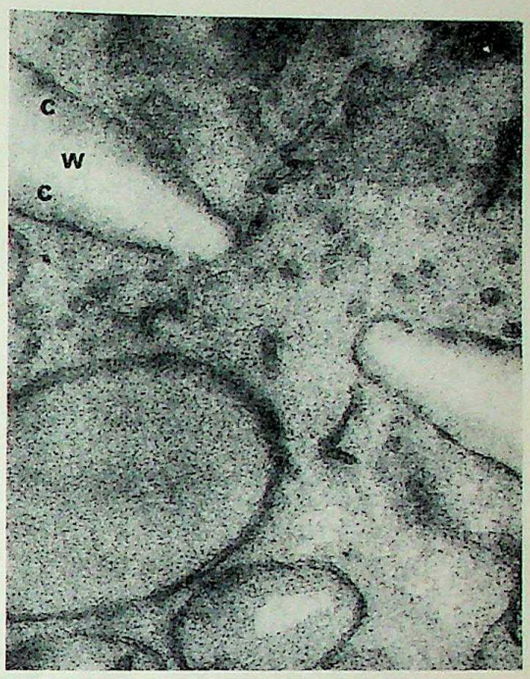

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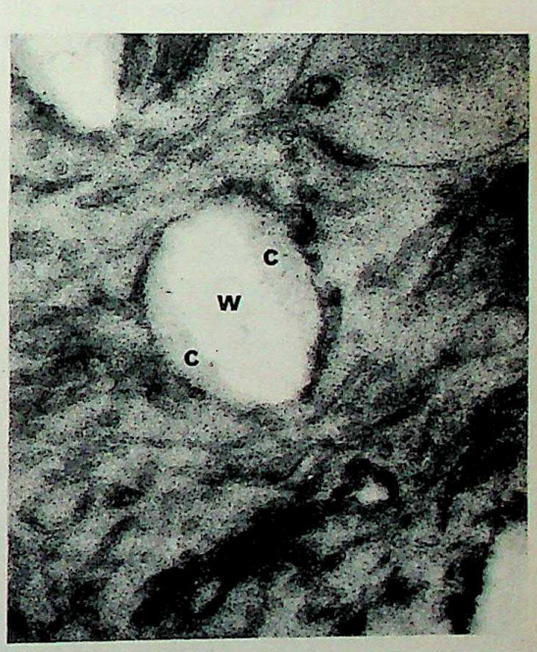

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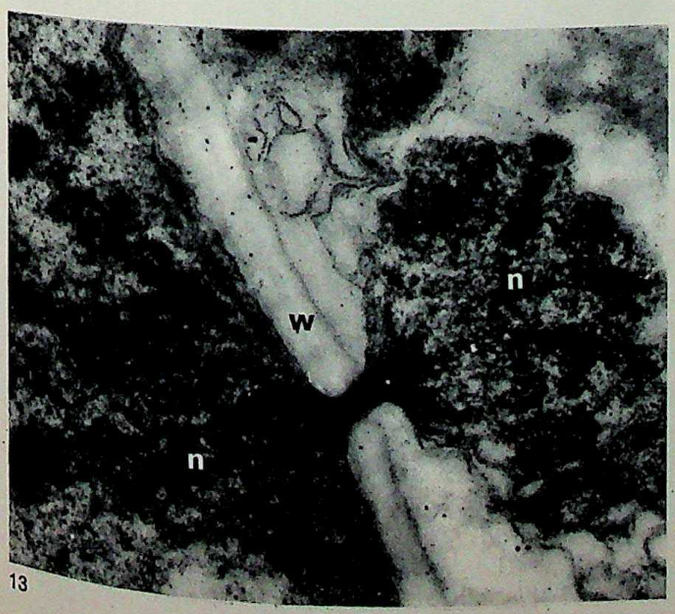

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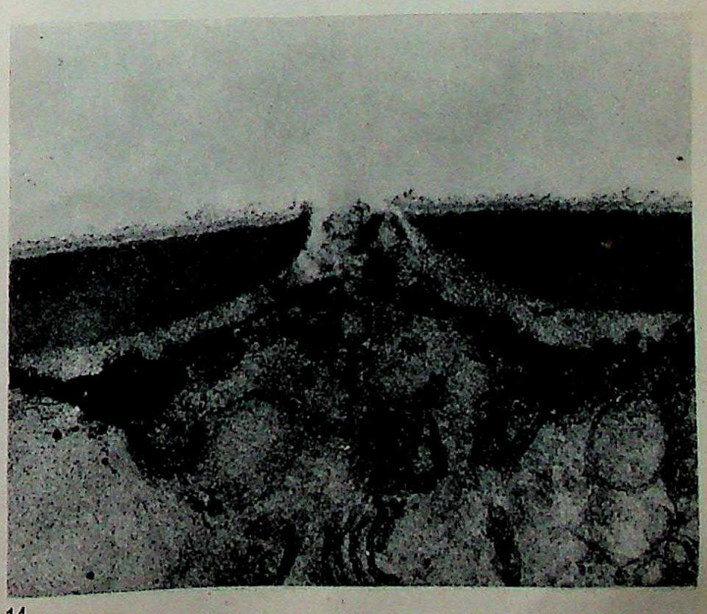

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interconnecting channels are some 40 times wider. Thus the total pathway for intercommunication is greater and offers a means of transfer for cell components that could pass between cells in no other tissue of the plant body apart from the phloem. The transfer of whole nuclei or nuclear fragments—Gates's cytomixis—probably never occurs in the intact archesporium. DNA movement among prophase meiocytes of *Lilium* has been studied by S. Takats [19], who has found that transfers occur mostly during zygotene-pachytene and that the incidence of movement is increased by wounding. Moreover, when injury is localized, the direction of DNA movement is polarized towards the site, strongly suggesting that the whole effect results from the wounding. In orchids like *Dactylorchis fuchsii*, meiocytes of which are illustrated in figure 9, the pollen is formed in packets or massulae within the anther. Cytoplasmic community exists during prophase among the meiocytes of a single massula, but not between massulae. However, groups of massulae can be fixed and processed for electron microscopy without the mechanical disturbance to individuals that anthers normally suffer, and in this case, nuclear movement between meiocytes of individual massulae is never observed.

While nuclear transfer is not likely to occur in the intact archesporium (and it would indeed be disturbing if it were to be a regular feature of meiosis), there seems no doubt that organelles such as mitochondria and plastids may move between meiocytes, while continuities are certainly established between the endoplasmic reticulum of neighbouring cells. The picture thus emerges of the whole mass of mother cells sharing a common cytoplasm. No technique exists at present for determining whether transcellular cyclosis occurs during the meiotic prophase, but electron micrographs often give an impression of movement (figure 12).

One consequence of this degree of cytoplasmic continuity is obvious. When in any tissue adjacent cells assume independent behaviour in differentiation and division, it must be because their nuclei exert exclusive control within each over their own cytoplasm. The sharing of a common cytoplasm throughout the anther loculus will act to negate this kind of independence, and to impose co-ordinated behaviour. This suggestion is borne out by the close synchronization of the events of meiosis itself in all the linked spore mother cells. Even though this synchronization may not be perfect in large anthers because of the existence of slight timing differences between base and apex, the very existence of smooth gradients of this kind illustrates the extent of interaction.

While the cytoplasmic continuity between meiocytes synchronizes the meiotic behaviour, it is possible that the links fulfil another function in offering a pathway for the rapid movement of materials. This is considered further below.

As we have seen, with the total elimination of the intermeiocyte connections and the formation of the all-enveloping callose wall, there is no further cytoplasmic continuity between the microspores, or between them and maternal tissues, even through plasmodesmata. Just as the earlier cytoplasmic community imposed interdependence, so this new isolation offers cellular autonomy. The significance of this is perhaps best appreciated in relation to the angiosperm life cycle, discussed in the introductory paragraphs.

The microspore is the first cell of the haploid male gametophyte—a separate generation, notwithstanding its nutritional reliance on the parent sporophyte. In consequence of segregation, each nucleus of a tetrad may be different genetically from all others, and of course from the parent. Genes acting early in the life of the gametophyte will presumably do so by producing characteristic messenger RNAs, and it seems assured that the callose tetrad wall will effectively prevent the pooling of these.

An instructive demonstration of the effectiveness of the wall of the tetrad in affording functional autonomy is

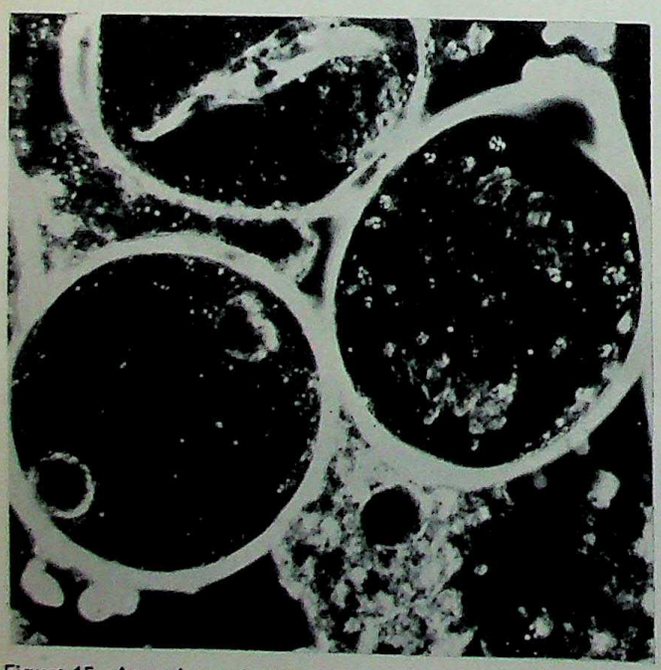

Figure 15 Asynchrony in the first meiotic division in neighbouring meiocytes of *Lilium henryi*. The cell on the left is in interphase; that on the right in anaphase. The preparation was made from a single anther loculus, and is viewed here in the living state by dark-field illumination. (×1000)

Figure 16 Asynchrony in the second meiotic division in a single meiocyte of *Lilium henryi*. The dyad has an equatorial wall of callose, unpenetrated by plasmodesmata at this time. The upper cell is in telophase, the lower still in metaphase. (×1700)

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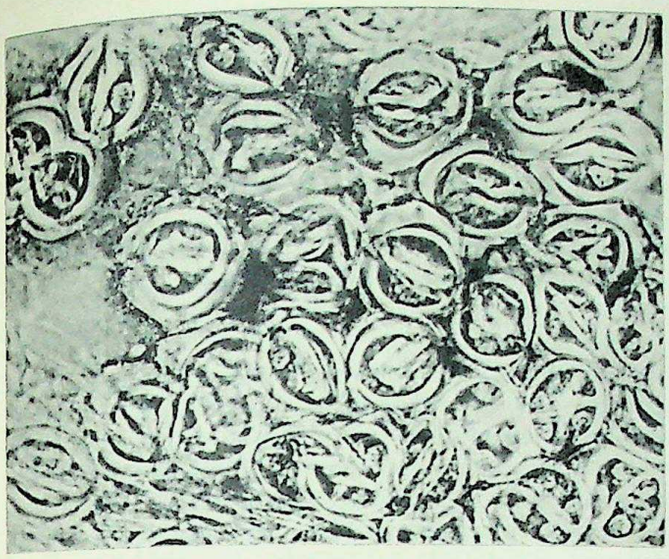

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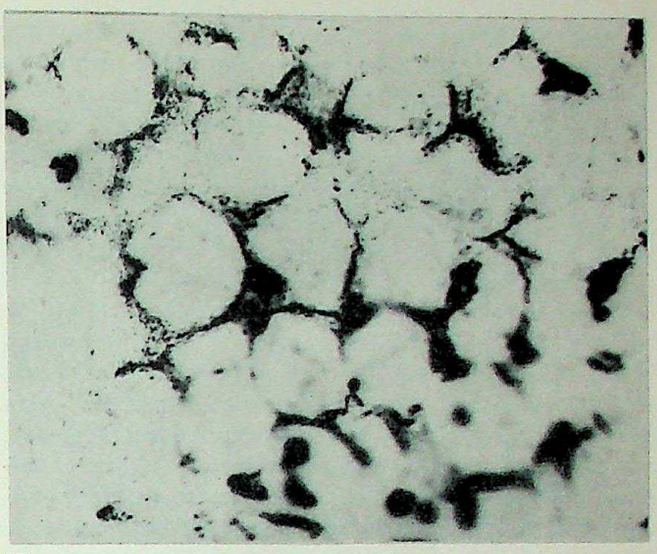

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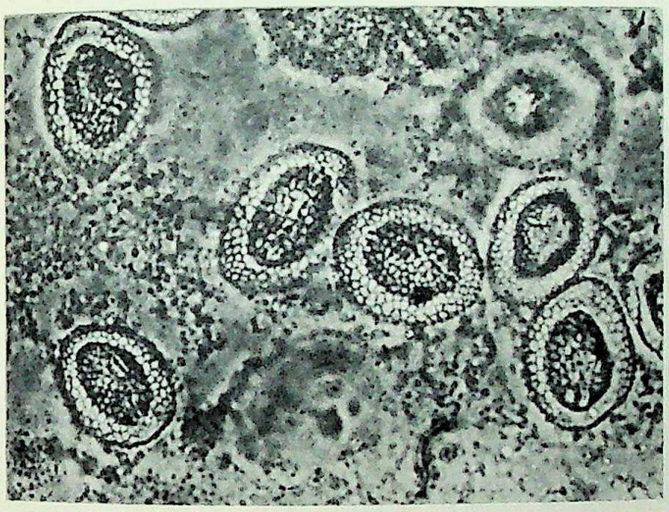

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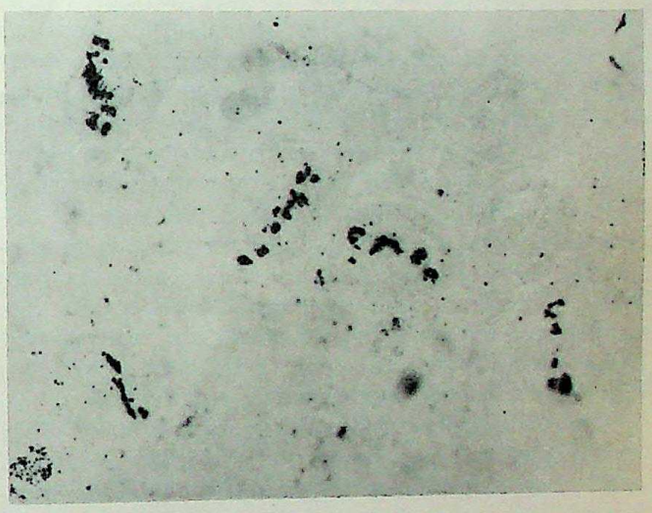

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Figure 17 Distribution of ^{14}C-labelled thymidine supplied to a *Lilium* anther when the inter-meiocyte connections were being severed: *a*, phase contrast image showing meiocytes; *b*, light-field image showing silver distribution. The tracer has reached the anther loculus, and is present in the scattered tapetal nuclei which appear as dark masses, and is also everywhere present between the meiocytes, which have progressed to the tetrad stage. There is, however, no radioactivity in the tetrads, suggesting that there has been no penetration. Most of the interstitial label can be removed by short-term acid leaching, but that in the tapetal nuclei is held, indicating that it has been incorporated in DNA. (×205)

Figure 18 A later stage in a similar experiment to that of figure 17. The tetrads have now dissociated, and the young spores have been released (phase contrast image, *a*). The distribution of silver (light field image, *b*) indicates that the tracer previously present between the tetrads has been avidly taken up by the young spores, most of which show strongly localized radioactivity. Again, since the label can be removed by leaching there has been no nuclear incorporation. (×600)

Figures 17 and 18 are from a study in collaboration with Mr A. Mackenzie.

given by the timing of the later events of meiosis itself. As we have seen, during prophase behaviour tends to be synchronous in neighbouring meiocytes. After the elimination of the cytoplasmic connections, the behaviour becomes progressively less synchronized. In *Lilium*, where the connections are severed relatively early, deviation in the timing of contiguous meiocytes is apparent as early as metaphase I (figure 15). Since a callose wall is formed between the interkinetic nuclei even before the second meiotic division, they come to lie in independent cytoplasms, and so the second division may be asynchronous in the two halves of the dyad (figure 16). In contrast, in plants like *Helleborus*, where a simultaneous cleavage of the meiocyte gives a tetrad direct without the intervention of a two-cell stage, synchronization is retained throughout the second meiotic division.

The function of callose for sealing and plugging has already been mentioned. It would seem, at first sight, that a degree of mechanical strength and an impermeability to macromolecules is all that is required for the discharging of the tasks assigned to wound callose [2] and to fulfil the role just outlined for the tetrad wall. It might be argued that such functions can as well be served by the intact plasmalemma backed by a cellulose wall, in which case the special value of callose would lie only in the speed with which it can be synthesized and broken down. However, a recent experiment indicates that the callose of at least the tetrad may be very much more impermeable than the normal cellulose wall.

In this experiment, buds of *Lilium* were supplied with ^{14}C-labelled thymidine over periods of microspore formation that included prophase stages and extended

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through the life of the tetrad to the release of the young microspores. In the usual autoradiographic techniques for the cytological localization of radioactive tracers, only the fraction incorporated in macromolecules can be detected, since soluble pools are leached out in processing. In the present experiment, the tracers in soluble pools were located by the application of extremely thin dry, loop-formed films of nuclear emulsion to dried smears of anther contents.

The resultant autoradiographs cast light both on the effect of the prophase inter-meiocyte connections and that of the callose wall. Tracer reaching the anther loculi at any time when the inter-meiocyte connections were present was distributed quickly throughout the whole mass of mother cells, and was retained within the meiocytes after the severance of the connections and the sealing of the callose wall. When the tracer reached the loculi after the sealing of the meiocyte walls following pachytene, it failed to enter. It was, however, accumulated in the cells of the nurse tissue, the tapetum, which surrounds the sporogenous cells, and appeared in the intercellular spaces throughout the meiocyte mass itself. This 'interstitial' label was often conspicuously evident in autoradiographs of the spread anther contents at the tetrad stage (figure 17). Following the dissolution of the callose tetrad walls, the released microspores speedily took up the tracer, and they then yielded a clearly localized autoradiograph (figure 18). The simplest—although not the only possible—explanation of these results is that while they are invested in the intact callose wall, the meiocyte and the young microspores are able to resist the penetration of even so relatively small a molecule as thymidine.

The possibility that the cytoplasmic connections of the meiotic prophase provide a pathway for the transfer of nutrients through the sporogenous tissue has been mentioned. This is an attractive hypothesis, since it may be argued that the initiation of the callose wall during the early prophase occludes the usual pathway of intercellular movement of solutes, which in a normal parenchyma diffuse through permeable cellulose. By increasing the area of direct contact, the cytoplasmic links more than make up for the lost areas for diffusion through the wall. If indeed the intact callose wall is an effective barrier against the penetration of many materials reaching the spore mass from its food source, an implication is that the meiocytes and their products must, from the closing of the wall towards the end of prophase until its final dissolution at the end of the tetrad period, be subsisting on reserves accumulated earlier. There is, therefore, certainly a 'requirement' for a high-capacity, rapidly-acting translocation system throughout the sporogenous tissue during prophase, particularly in massive archesporia, where the central meiocytes may be some distance from their source of nutrition. One current theory of solute translocation in the phloem is based upon the conception that the movement occurs in strands of cytoplasm passing from one cell to another [20, 21]; it may not be too far-fetched to suggest that the system in the archesporium supplies an analogy.

In conclusion, it is noteworthy that these various phenomena offer an explanation for the failure of attempts to culture sporocytes *in vitro* from early stages. Late meiocytes can be cultured to pollen grains in artificial media, but this has not proved feasible with mother cells extracted in early prophase. Evidently the cytoplasmic continuity in the archesporium means that damage inflicted during extraction is likely to be propagated to all its parts, so that subsequent survival of any of its cells *in vitro* is unlikely. However, it should be possible to culture self-contained meiocyte masses, such as the massulae of orchids, through the whole of meiosis.

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John Dalton

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Frank Greenaway

The bicentenary of the birth of John Dalton, the originator of the chemical atomic theory, is to be celebrated this year. The atomic theory current in the eighteenth century has already been described in the last issue of this journal: Dalton's theory differs markedly from this. There are a number of accounts of the way that his theory developed, and these are critically discussed in this article, which also describes what is known of the main events in Dalton's life.

John Dalton, who was born on 6th September 1766 and died on 27th July 1844, made a contribution to science of great significance [1]. The belief that matter was composed of atoms had been discussed since ancient times, but it remained speculative, as a recent article in ENDEAVOUR [2] has shown, until the beginning of the nineteenth century: by this time, the reactions of chemical substances had been put on a quantitative basis. Dalton brought atomism and quantitative chemistry together, showing how some microscopic properties could be inferred from macroscopic measurements, which themselves could be deduced from a theory of microscopic constitution. This was Dalton's atomic theory. An account of the atomic theory of his contemporary, William Higgins, has already been published in ENDEAVOUR [3].

The effects of Dalton's theory were widespread. All inorganic chemical analysis was given a rational basis, since the theoretical composition of substances could be predicted and compared with experimentally determined values; and the self-consistency of inorganic analysis affected industrial progress as well as research. The results of organic analysis could be related to inorganic analysis, thereby preparing the way for the unification of the two branches, and also for the development of theories of organic chemistry expressed in atomic terms.

Dalton pictured an atom of an element as a sphere surrounded by an 'atmosphere' of heat (thought of as a subtle fluid, 'caloric'), which played a role in many physical changes [4]. A compound of element A and element B was made up of 'compound atoms', each consisting (in the simplest compounds) of one atom of element A and one atom of element B [5]. More complex forms were envisaged. This simple concept of indivisible spherical atoms served chemistry and physics well for interpreting many phenomena. In spite of fundamental modern advances in the theory of the structure of the atom, the Daltonian spherical atom is the basis of innumerable molecular structure models that still serve very well for many purposes.

One use of the simple sphere picture—the kinetic theory—was not in Dalton's mind. Bernoulli's kinetic theory had been overlooked, and Dalton, like his contemporaries, thought of the structure of fluids as static: even diffusion of one gas into another was considered by Dalton to be a movement of atoms to take up fixed positions. In fact, one of the origins of Dalton's great conception was an attempt to discover the conditions of gaseous equilibrium.

Frank Greenaway, *M.A., M.Sc., F.R.I.C.*
Was born in Cardiff in 1917 and was educated at Jesus College, Oxford, and University College, London. In 1949 he was appointed Assistant Keeper in the Science Museum, South Kensington, becoming Deputy Keeper of Chemistry in 1959. His chief work is in the study of the history of analytical chemistry and of representations of theories of chemical constitution. He is a corresponding member of the International Academy of the History of Science.

Dalton's early work

Dalton's childhood was short and he soon started work. Although isolated, physically, in the country—he lived in the hamlet of Eaglesfield in Cumberland—he was not entirely remote from cultural influences. Dalton was a Quaker, which ensured a good elementary schooling. He tried his own hand at teaching for a time while only twelve years old, and then worked on the land; at fifteen he left Eaglesfield for Kendal, some forty miles away, taking once again to teaching and remaining a teacher all his life. Of all Dalton's personal papers, the most revealing of his character are his account books, in which he set down the fees he received for classes and lectures and his expenditure on the books and apparatus he needed. Taken with the meteorological notebooks, which he kept without a break every day of his life from 1781 onwards, they give a vivid picture of his life at Kendal. The account books show that there was always a good initial enrolment, but that attendance dropped off rapidly; many people came to only the first lecture of a set, and only a faithful few held on. Even reducing the price by half—to five shillings for twelve lectures—failed to improve attendances. However, he did impress scholars who met him, notably the phenomenal John Gough [6], who, although blind from infancy, did useful work in physics and mathematics (William Whewell was one of his pupils). His opinion of Dalton was so high that, in 1793, Gough was able to recommend him as tutor in mathematics at the New College in Manchester (a successor to the Dissenting Academy at Warrington). Here he was already well known to scientific circles as a visiting lecturer. Whatever the shortcomings of the rough, gruff manner of his lectures, the matter was of more consequence to the educated circle of Manchester than to that of Kendal. The Manchester Literary and Philosophical Society was already an important feature of the city's life [7], with men of many callings as its leaders. They included the far-sighted, successful chemical manufacturer Thomas Henry [8], characterized by his remark in the first volume of the Manchester Memoirs: 'The pity is that more chemists are not dyers and more dyers are not chemists'. They were conscious of the need to be strengthened by men of scientific action, capable of experimental originality, and Dalton was already on the point of publishing work which, if it was not to be a resounding success, at least would establish him as a respectable scientific author.

Meteorological observations

Dalton's *Meteorological Observations and Essays* [9] has never been treated as a work of any significance because it describes no new fundamental discoveries. His greatest contribution to meteorology was not made until eight years after this publication, but the book tells us a good

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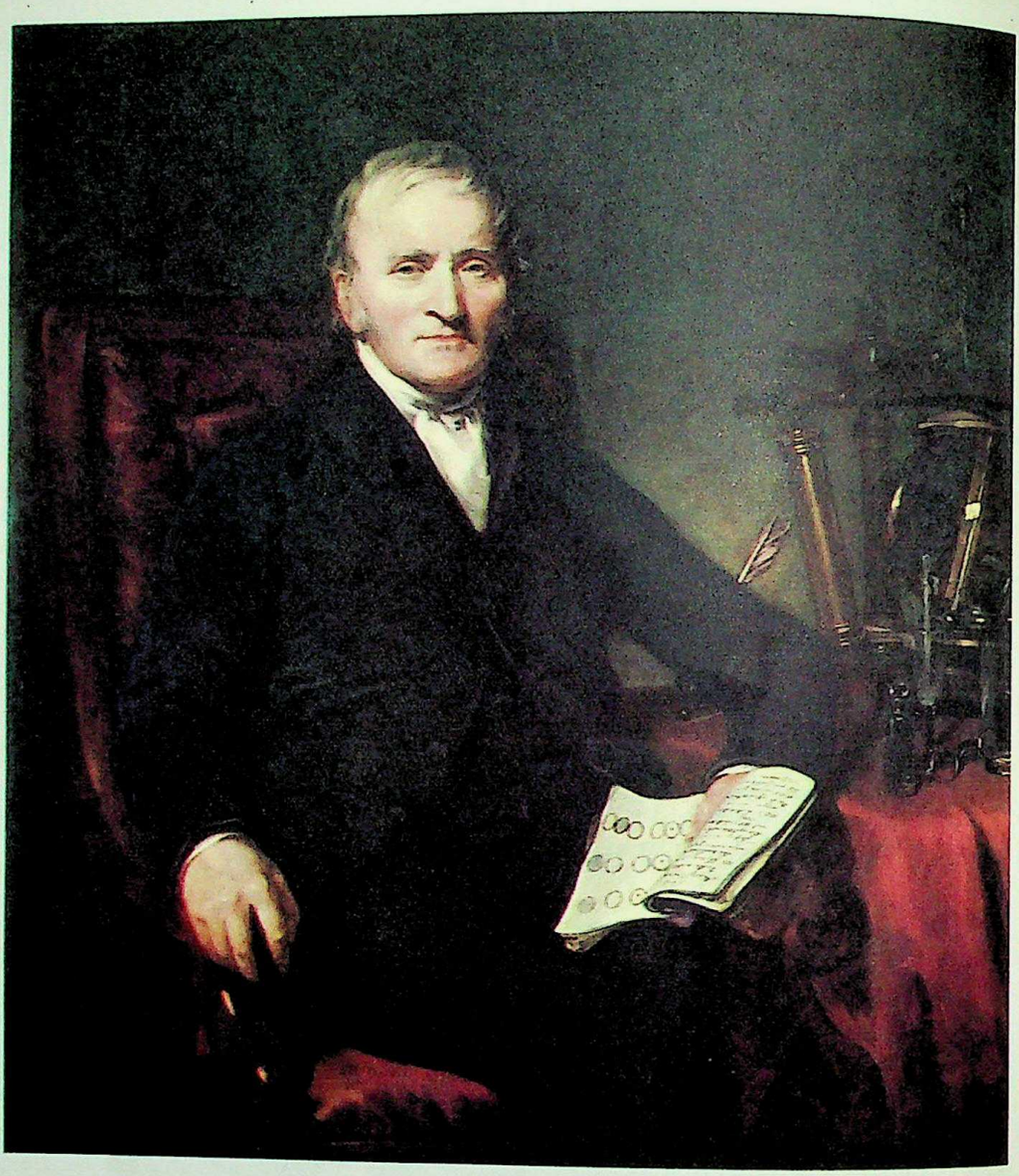

Figure 1 John Dalton, by B. R. Faulkner. (By courtesy of The Royal Society.)

deal about the range of problems which faced the scientific world of 1793.

Dalton had set out, he says, to give simple instructions to people who, interested in amateur observations and experiments, wanted to make their own simple instruments. While composing descriptions of the barometer, thermometer, hygrometer and rain gauge, he felt it necessary to add some theories of his own on such subjects as the origin of winds and the nature of the aurora borealis.

The often-repeated legend of Dalton's disregard of books is untrue. Dalton was not contemptuous of books, but was sadly deprived of them in his early years. He was quick to use them when he got to the libraries of Manchester, after his own first book was already in proof form, and to acknowledge in preface and footnotes the disconcerting discovery that some of his ideas, such as his theory of trade winds, were not new. The repertoire of problems in the book is wide. The very origin of the book is a reminder that the management of instruments was by no means uniform or standard. Although there were many excellent instrument-makers at work, there was still little feeling of any need to achieve concordance between the instruments used by one investigator and another. Even if there had been, many amateurs would still have needed to make their own, or even preferred to, using instructions like those set out by Dalton. The book was conceived as an aid to the amateur philosopher: it grew into a work containing the beginning of Dalton's scientific ideas.

Although chemical weight determinations were paramount in Dalton's later thought, they were quite absent from this early work. The balance plays no part in Dalton's meteorology. However, he was concerned with the problem of the composition of the air, and with one aspect of it—is the water that is contained in atmospheric air chemically combined or only physically admixed?

From ancient times the atmosphere had been interesting to scholars; as a fluid it had become even more interesting to the experimenters of the seventeenth century; and as a gas accessible to chemical experiment the eighteenth century found it a challenge of the greatest theoretical consequence. The major issue for the future development of systematic chemistry was the nature of its main constituents, but even after Lavoisier had shown that air was mainly a two-component system of constant proportions, it was still not clear whether the components were united by chemical affinity or merely intermingled. Similar doubts applied to the water that was present in air in variable amounts. Dalton had lived, in his beloved Lake District, very close to the weather; he could not help being intensely conscious of the coming and going of water in the air; he noted the interference of the water vapour from a wet leather valve with results obtained with an air

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Figure 2 Coloured threads of silk used by Dalton and Sir John Herschel in colour-blindness tests about 1830. (Crown copyright. Science Museum, London.)

pump. If there is any one link more important than another between Dalton's early experiments and his great inspiration, it is to be found not in the traditional particle ideas or in Newtonian atomism or in studies of chemical composition, but in this problem of the nature of atmospheric water vapour.

Dalton's contributions to physics

Dalton took some time to produce anything really important in physical science, if we exclude his paper of 1794 on colour vision. This was a minor masterpiece in which, colour-blind himself, he was able to show that the phenomenon of colour-blindness existed, and unlike the one or two previous reporters of colour vision anomalies, to show that it was accessible to exact study [10]. He matched coloured cloths by daylight and candlelight, compared his matches with those made by his brother and by his friends, tested a family in whom anomalous colour vision had already been reported, and produced an ingenious (if erroneous) physiological theory to account for the phenomenon (figure 2).

In 1799 he read another paper [11] for which he has received too little credit, on the study of the origin of springs—the first serious attempt to consider a large-scale problem of natural resources in quantitative and experimental terms. He showed how to compute the total rainfall from separate data, and the total run-off over the whole country from studies of the speeds of current in typical rivers. He thence argued that springs arise from stored rainfall, rather than from a permanent reservoir of subterranean water (figure 3). From the hydrological cycle he turned to the thermal properties of water, refuting, by experiments of delightful simplicity, Count Rumford's theory that fluids cannot conduct heat; for example, he put a hot bar in the top of some water in a tall jar, and showed there was a rise of temperature at the bottom even though there could have been no convection [12].

Then came some fine work, bringing him an international reputation: he showed that the pressure of a mixed gas is the sum of the pressures of the components (Dalton's Law of Partial Pressures) (figure 4), and at the same time he found the law of thermal expansion of gases. This is universally known as Charles's Law, which is hard on Dalton because although Charles had anticipated him, his work was not published until after Dalton's. So far particle ideas played little part in his expositions, but they were necessary for his pioneer work on diffusion.

The origin of Dalton's atomic theory

In the first years of the century he was developing two other enquiries, and it has long been a matter of dispute as to which, if either, led him to his atomic theory. One was into the proportional composition of the atmosphere. He used the test for the goodness of air devised by Priestley (the reaction between nitric oxide and oxygen with absorption of the water-soluble products), and some of the results were later shown by Dalton himself to be concordant with what came to be known as the Law of Multiple Proportions. The other investigation was into the absorption of gases by liquids—the converse of the problem of the absorption of water by air (figures 5–7). It was at the end of the paper on gas solubility [13], read on 21st October 1803 (but not published until 1805), that there appears the famous passage:

> 'An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting it with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin my results, as far as they appear to be ascertained by my experiments.'

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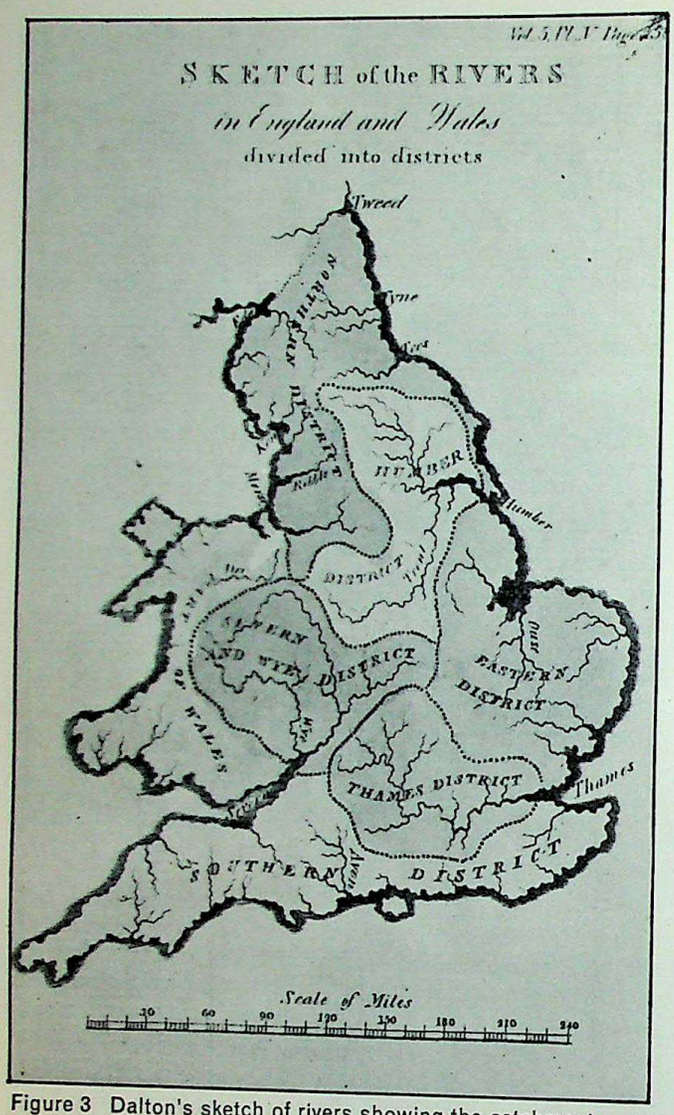

Figure 3 Dalton's sketch of rivers showing the catchment areas from which he calculated total rainfall and run-off.

There follows a 'Table of the relative weights of the ultimate particles of gaseous and other bodies'—the first table of atomic weights. This table was the product of a far-reaching theory of chemical constitution, first published by Thomas Thomson in a textbook in 1807 [14] that refers to conversations Thomson had had with Dalton in 1804. The effect on some readers was profound.

In January 1808, the Royal Society heard from Thomson and from Wollaston papers on the oxalates [15] in which Dalton's ideas were the central feature. Wollaston, indeed, seized on them with such vigour that he may well have been on the point of propounding some such theory himself. Between them they showed how the theory explained the occurrence of pairs of compounds of the type $AB;AB_2$. Long after, in 1830, Thomson alleged that Dalton had based his theory on studies of multiple proportions in hydrocarbons. W. C. Henry, the first biographer of Dalton, in 1854, reported his father's recollection of Dalton referring to an indebtedness to Richter's work on equivalents, but Henry questioned the reliability of Dalton's own memory. Later biographers repeated the view that Dalton had argued from cases of Multiple Proportions. In 1896, a new view was put forward by Henry Roscoe (quoted in [16]), based on a correlation of Dalton's notebooks (which had been discovered in the rooms of the Manchester Literary and Philosophical Society, where Dalton had done most of his work) with his published statements. Roscoe concluded that Dalton had been intent on solving, by considering the sizes of particles, the physical problem of why a mixture of gases of different densities does not separate into two layers. The chemical aspect, that is to say, was almost incidental. In 1910–11, A. N. Meldrum produced support for a mainly chemical turn in Dalton's mind, pointing to the studies of the oxides of nitrogen in the course of the work on the composition of air. As recently as 1956, L. K. Nash reopened the question by emphasizing Dalton's studies of gas solubilities. The author's own view, based on Dalton's early obsession with water vapour, and supported by the recent discovery of a lecture syllabus of 1805 which seems to have escaped notice, is that Dalton wanted to satisfy himself about the properties of water, and that the realization that he could calculate the atomic weights of its components led him to the atomic weights of other substances. The elucidation of the composition of water was as important in the establishment of the anti-phlogistonist system of chemistry as had been the elucidation of the composition of air: Dalton may well have seen this as a problem on which there was new light to be thrown. Whatever the first specific instance of the theory, the generalization followed rapidly enough for Thomson to hear it from Dalton's

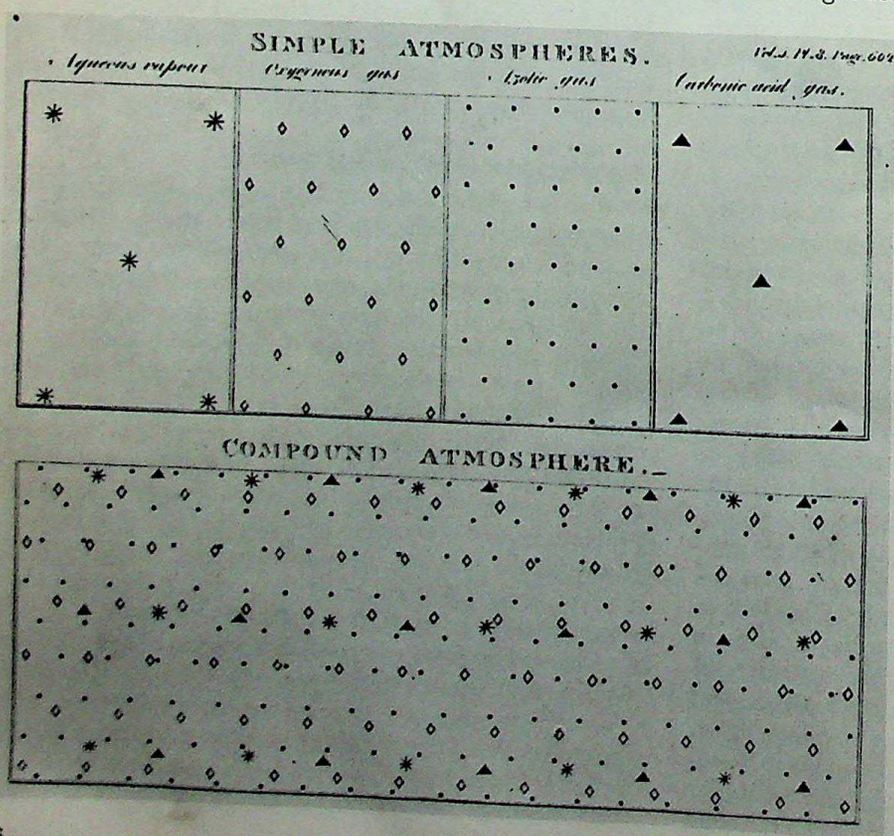

Figure 4 Dalton's diagram showing particles of several gases occupying the same space without exerting any force upon any but their own kind, each behaving as if it were in a vacuum. [17]

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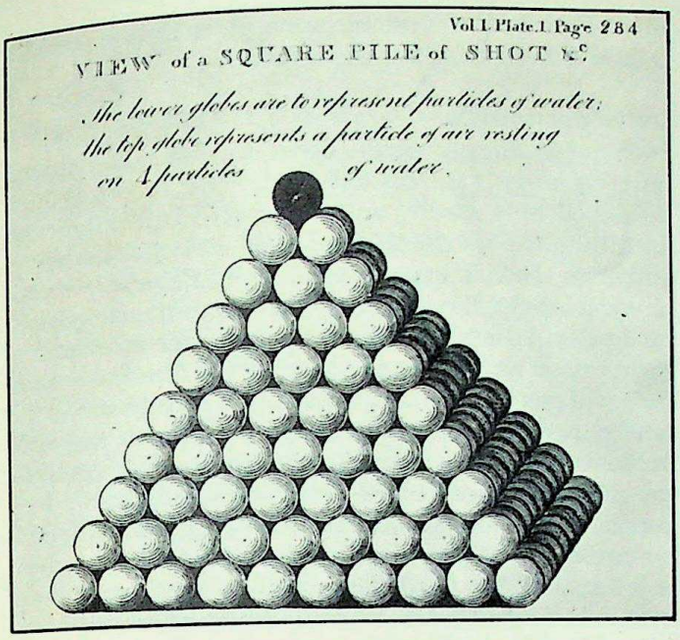

Figure 5

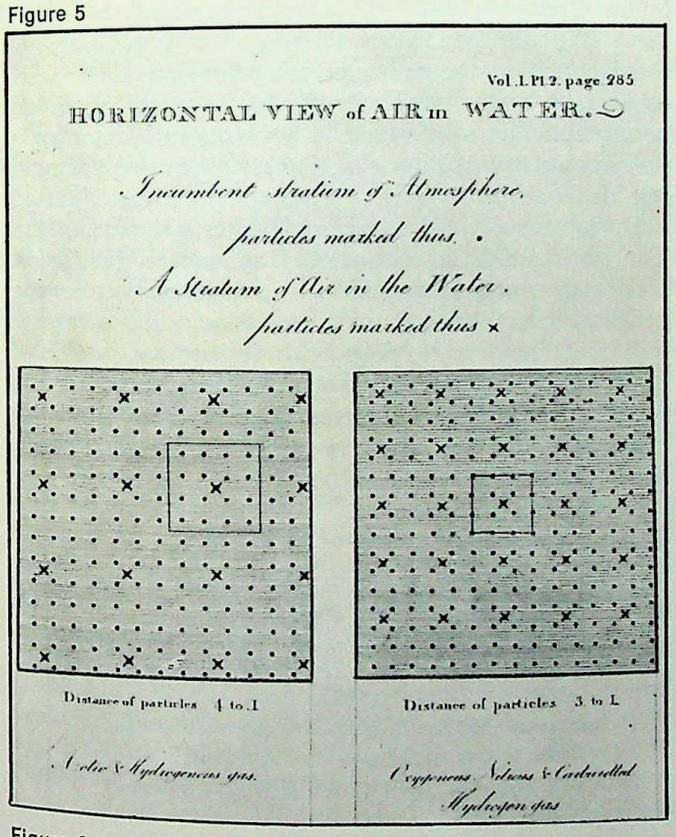

Figure 6

Figures 5–7 Examples of Dalton's early thoughts on dissolved gases (1803) [13]

Figure 5 View of square pile of shot: Dalton's analogy to show how pressure is distributed according to an inverse square law.

Figure 6 Horizontal view of air in water. This is a plan view showing the inverse square law of pressure distribution, one layer on top of another.

Figure 7 Profile view of air in water. The inverse square law operates so as to bring the pressure on top of a layer of dissolved gas into equilibrium (through intervening water particles) with the external gas.

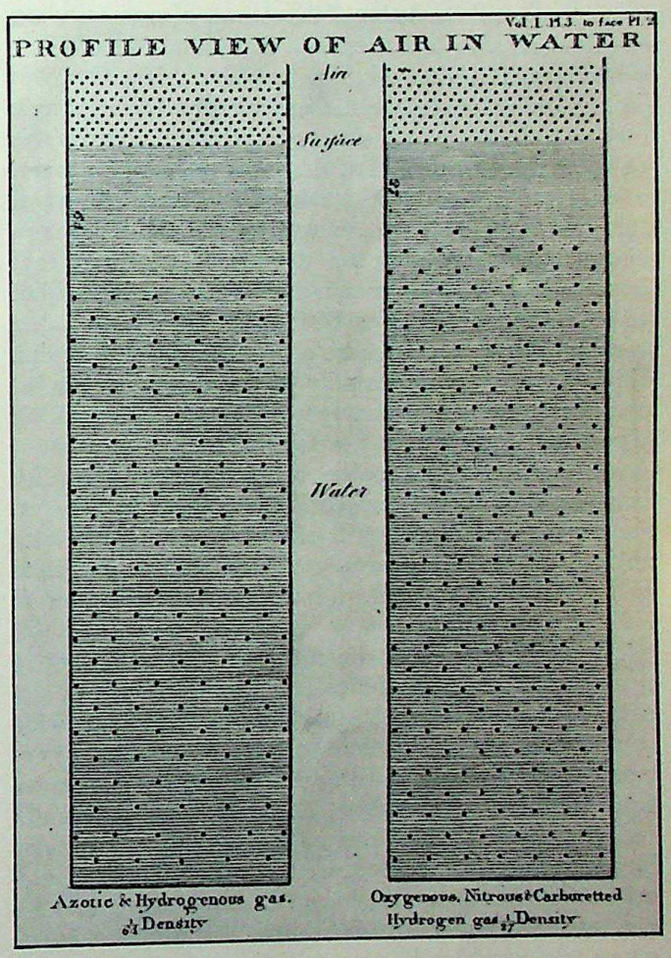

Figure 7

lips in 1804, and Dalton himself seems to have expounded it in his Royal Institution lectures in 1803–4. He set out the essentials with superb clarity in the few important pages of a large book which is otherwise of indifferent merit. Encouraged by his Manchester friends and by a warm reception in Scotland, he embodied his lectures in a *New System of Chemical Philosophy*. The first part, published in 1808, was mainly an account of the theory of heat and of the three states of matter, using exposition in terms of particles far more often than he had done in any previous work. The last chapter of this part contained the atomic theory, expressed as a theory of combination. It was not necessary for him to postulate here that the atoms of an element are all alike; he had already shown this from purely physical considerations, such as that a gas made of different sized particles would separate into different layers. The sound conclusion, though drawn from unsound premises, leads him to assert 'the importance and advantage of ascertaining the relative weights of ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.' He assumes that the simplest compound between element A and element B must be of the form AB. Therefore, the relative weights of the ultimate particles (atoms) of A and B are as the proportional composition by weight of the compound AB. More complicated cases are considered, such as compounds of the form AB_2, etc. This was all for the time being. By the time Part 2

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appeared in 1810, the theory was in use in other hands and Dalton had nothing remarkable to add. Part 2 was an attempt at a general chemical textbook, but it dealt with only a fraction of the field. Volume 2 appeared in 1827, almost apologetically prefaced with the remark that it was more an account of the author's own experiments than a textbook. Dalton was never very wise about publication; he had too little regular contact with the bigger world of science, of which Manchester could be no more than a fringe, to benefit from the growing modernization of publication. He could write clearly and informatively on a small scale, but in long works he faltered.

The consequences of the atomic theory

The dispute about the origins of Dalton's theory should remind those who are not historians of science of the uncertainty of our knowledge of the sources of many modern scientific ideas. It does not mean that Dalton was clumsy or haphazard in his work, nor that his achievement was any the less valuable because we cannot attach a simple story to it. Certainly, the effect on his contemporaries was considerable. In the field of theory, it appeared at once, to some, to be connected with Gay-Lussac's Law of Volumes, to which it bore so close a resemblance: Dalton rejected the connection on the realistic ground that simple relations in the treacherous experimental field of gas reactions were likely to be illusory. He rejected what we now know as Avogadro's hypothesis for a reason which might well exemplify the whole problem of advance in scientific conceptual thought: Avogadro's hypothesis required that the simplest entity in a gaseous element should be capable of division (so that, for example, the units of oxygen shall be divisible between the twice as numerous units of hydrogen to form water units). Dalton, having postulated an atomic entity as the unit of an element, could not accept questioning of its indivisible atomicity.

The realization that the future of chemistry lay in extension of exact analytical data, without which decisions about atomic weights and molecular composition could have no validity, led Berzelius to the great programme of analyses which gave chemistry a massive background of reliable data. The excellence and significance of his successive determinations of atomic weights illustrate the power of Dalton's theory to energize chemical enquiry. It is a paradox of Dalton's work that his greatest influence was in a field of chemistry, analytical chemistry, in which he was undistinguished.

The atomic theory of Dalton, providing any substance with a theoretical composition with which practical analytical results could be compared, gave analysis the orientation it had hitherto lacked. To academic analysts like Berzelius, and applied analysts like Heinrich Rose, the atomic theory gave an interlocking system of weight relations. It is sometimes said that Dalton's atomism gave way to the system of equivalents favoured by Wollaston in which many analytical results were expressed. This is unfair to Dalton, since the later system, while superficially as empirical as that of Bergman, depended upon the continual appeal back to discussion in atomic terms.

The rise of quantitative control in industrial chemistry, the entry of analytical chemistry into public welfare controls, the eventual codification of combining properties in the related systems of valency and classification, these all evolved from the atomic concept of Dalton, even if Dalton did not originate them directly.

Dalton's personality

Such achievements would seem to define a man of towering intellect and masterful character. In fact, Dalton developed only slowly, and made no mark on science until he was over thirty. He lacked Berzelius's sense of authority, Davy's experimental flair, Faraday's metaphysical insight, Lavoisier's capacity for organizing information, and Liebig's sense of educational mission. His early papers and the first volume of the *New System* have flashes of genius. The rest of his work is pedestrian; the later papers and later parts of the *New System* look old-fashioned. Yet he was much admired in Manchester—too much admired indeed, because he was lionized by people who could have had little means of estimating his real worth. He deserved the Oxford degree he was given in 1832 and his Civil List pension of 1834, but the hysterical funeral given to the quiet Quaker was, as his fellow Quakers protested, an insincere parade. For forty years after 1804 the Dalton who had brought the ancient atom back into the centre of scientific thought went on as he had begun, teaching elementary subjects to the young and the uninformed in private, and lecturing in public on many scientific subjects, meteorology remaining his favourite.

In one respect his admirers felt he had failed them. The testimonials in support of a memorial referred to his detachment from applied science. His early colleagues had hoped for a scientist who would carry his talent into mill and factory, helping with immediate problems. However, apart from occasional analyses, he did nothing to aid particular manufactures. Even so, Manchester was content to have been the chosen home of a great man.

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Mass spectrometry in organic chemistry

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J. H. Beynon

Mass spectrometry is a technique with its origins in the work of physicists in the early years of this century, but it has only recently become possible to apply the method to the routine analysis of organic compounds. This article describes the technique and the instruments it uses, and shows how it can be used to resolve problems in structural chemistry that are otherwise insoluble.

The first crude mass spectra—spectra of positive ions—were produced by W. Wien [1] and by J. J. Thomson [2], when they were examining the nature of the positively charged ions in low-pressure electrical discharge tubes. Thomson's experiments, performed in 1910, were the more refined; a beam of ions was passed through combined electric and magnetic fields so that the ions produced a series of parabolic curves on a photographic plate. Each curve corresponded to ions of a particular mass-to-charge ratio, and Thomson made the noteworthy observation of a line corresponding to a mass-to-charge ratio of 22, later shown to be due to an isotope of neon. Instrumental developments to study isotopes quickly followed along two lines. A. J. Dempster [3] developed an instrument in which an essentially mono-energetic ion beam could be produced by bombarding a gas at low pressure with electrons, followed by acceleration of the ions so produced to high velocity by means of an electric field. The ion beam was separated by means of a magnetic field into a series of beams, each containing ions of a particular mass-to-charge ratio. The relative abundance of each ion species could be determined by measuring the corresponding ion currents electrically, so that isotopic abundance ratios, for example, could be measured. Simultaneously, F. W. Aston [4] developed an instrument giving better resolution of the ion beams and far greater accuracy in the measurement of the masses of the individual isotopes. However, the beams were too weak to be measured electrically and had to be recorded on photographic plates. By 1924, isotopic mass and abundance values were available for about 50 of the elements.

Thomson appreciated the possibility of using mass spectra as a means of analysing chemical substances, but at first chemists were deterred from applying the technique to their problems. However, O. Eisenhut and R. Conrad [5] did use the parabola spectrograph to investigate the behaviour of methane, ethane, ethylene, and acetylene in a discharge tube. In all cases, they found ions corresponding to the breaking up of the molecules into all the possible simpler combinations, down to the ions of the elements.

Then, in 1940, H. Hoover and H. W. Washburn [6, 7] used a commercial version of Dempster's mass spectrometer to determine quantitatively the constituents of a complex hydrocarbon mixture. They used mass spectra of pure samples of all the constituents in these mixtures as references in analysing the mass spectrum of their mixture. Soon after this, mass spectrometers were established in petroleum refineries as continuous analysers and for process control; with the aid of computers, mixtures containing more than 40 components could be analysed.

Figure 1 is a diagram of a modern mass spectrometer as used in organic chemistry. The sample is ionized by a stream of electrons in the ion source, and the current that the ions carry is amplified and recorded.

Determination of structures

By studying the large numbers of hydrocarbon mass spectra which were being produced, organic chemists began to realize that the technique was likely to prove invaluable for the identification of organic compounds of other types: not only did the bombarding electrons used (usually of energy 50–100 eV) produce a wide variety of ions, but the so-called cracking pattern—the nature of the fragments formed—was uniquely dependent on the structure of the bombarded molecules. In addition, the mass spectrum usually contained a peak due to unfragmented molecular ions, from which the molecular weight of the sample material could be determined.

This molecular weight can be used to limit the number of possible molecular formulae for an unknown compound. For example, a molecular weight of, say, 84 can be satisfied only by a limited number of molecular formulae. If, for simplicity, one assumes that the unknown compound contains only atoms of carbon, hydrogen, nitrogen, and oxygen, then the only formulae which satisfy the molecular weight are C_6H_{12}, C_5H_8O, $C_4H_8N_2$, $C_4H_4O_2$, or $C_3H_4N_2O$. It is then necessary to decide which of these formulae corresponds to that of the unknown. Now each peak in a mass spectrum is accompanied by a series of smaller peaks at higher mass numbers, because there is a finite probability that molecules will

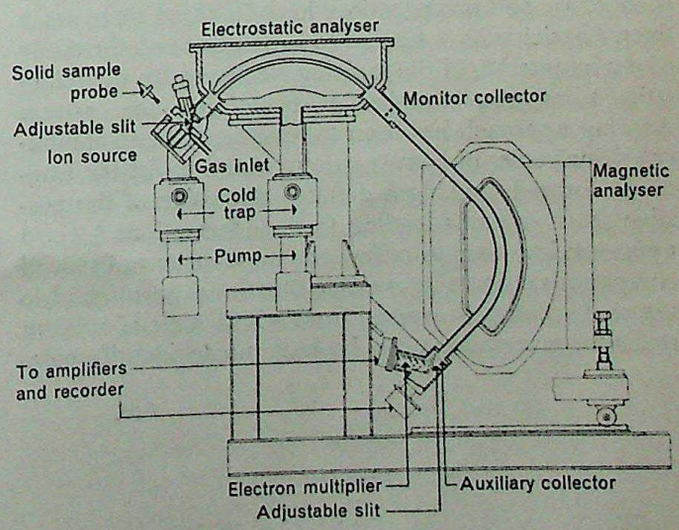

Figure 1 The MS9 double-focusing mass spectrometer made by Associated Electrical Industries Ltd. It can give a resolving power of about 25 000. It needs a vacuum of some 10^{-8} torr to prevent spread of the ion beam due to collisions with neutral gas molecules.

J. H. Beynon, *B.Sc., D.Sc., F. Inst.P.*
Was born in 1923 and educated at the University College of Swansea. Since 1947 has worked for the Dyestuffs Division of Imperial Chemical Industries Ltd, where he is Manager of the Physical Chemistry Division of Research. He is an ICI Senior Research Associate and has recently been appointed as first Fellow and Lecturer in Chemistry of the University College of Swansea.

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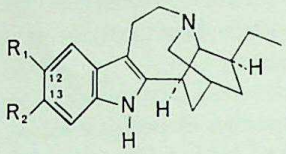
contain ^{13}C, D, ^{15}N, ^{17}O, or ^{18}O—the heavier isotopes—and this leads to molecular ions (for the above example) with masses of 85, 86, and even higher. For the hypothetical formulae quoted above, a peak of height 100 units at mass 84 would be accompanied by a peak at mass 85 of height 6·7, 5·6, 5·2, 4·5, or 4·1 units respectively because of the differing natural abundances of the heavy isotopes of the elements. Thus, by reference to a computed table [8] of formulae and corresponding isotopic abundances, the actual formula of the unknown can be determined.

In order to gain information about the structural formula, the fragment ions in the mass spectrum must be studied; but the difficulty then is that fragment ions of more than one formula can contribute to a peak at a particular mass number. Thus, from the compounds listed above, it might be possible to obtain fragment ions of formulae $CO^{+\cdot}$, $N_2^{+\cdot}$, CH_2N^+ and $C_2H_4^{+\cdot}$ all having a nominal mass of 28. However, because of the different packing fractions of their nuclei, the accurate masses of these combinations are all different, being respectively 27·994914, 28·006147, 28·018723, and 28·031299 u, and it is thus possible to separate them if the resolving power be sufficiently high. J. Mattauch and R. F. K. Herzog [9] demonstrated in 1934 many arrangements of electrostatic and magnetic fields capable of giving the necessary resolving power, and developments in electronics had by then increased the sensitivity of detectors so as to make it possible to record ion currents electrically, even under conditions of high resolution. Several commercial instruments are now available with which ion multiplets such as that illustrated above at mass 28 can be separated (figure 2, for example, contains a peak additional to those mentioned above, which corresponds to ions of formula $^{13}CCH_3^{+\cdot}$). The accuracy of such machines makes it possible to determine formulae of ions directly from their masses, with the aid of an appropriate table [8]. It is often possible to determine a molecular formula directly from an accurate mass measurement alone; isotopic abundances can still, of course, be used to confirm this formula.

Prediction of mass spectra

The prediction of the main features of a mass spectrum demands a knowledge of the fragmentation processes themselves, and investigations have followed three main lines. Physicists have tended to concentrate on the study of the interaction of the ionizing electron with the molecule, using small molecules containing few atoms. Another approach has been to investigate more complicated molecules of known structure and to list the fragments formed, making a detailed discussion of the possible reaction paths leading to their formation. A third approach has been to collect the mass spectra of several compounds containing a single functional group, and to search for common trends, from which a set of rules or structure correlations can be built up to identify compounds of the same class that are closely related. This last approach has proved particularly effective for natural products. For example, K. Biemann and M. Friedmann-Spiteller have given [10] the mass spectra of three of the alkaloids from *Tabernanthe iboga* which occur in nature in various degrees of methoxylation. Using the spectra of



Ibogamine	$R_1 = R_2 = H$
Ibogaine	$R_1 = CH_3O$; $R_2 = H$
Tabernanthine	$R_1 = H$; $R_2 = CH_3O$
Ibogaline	

ibogamine, ibogaine, and tabernanthine as references, they were able to deduce that the spectrum of ibogaline showed it to be a 12,13-dimethoxy ibogamine. There are many other examples in the literature in which subtle structural features have been elucidated by studying a series of related compounds. The spectra of these alkaloids are shown in figure 3.

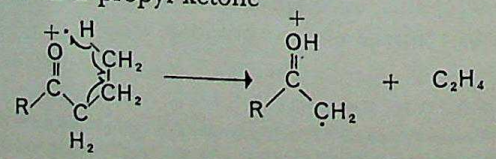
The origins of mass spectra

The only theory put forward to explain the nature of mass spectra is the statistical one [11]. In this it is assumed that any one of the valence electrons can be removed from the molecule with equal probability by the bombarding electron; that the excess energy imparted in this way to the molecule is free to travel throughout it; and that whenever sufficient energy is concentrated in a particular bond, the bond will break. Mass spectra of molecules as complicated as n-butane have been calculated on this basis, and found to agree well with experimental spectra, but the theory has had little success with molecules as complicated as those presently being examined by organic chemists, and so it will not be discussed here.

When a complicated molecule is disrupted, there is considerable evidence that whichever electron is actually removed during the ionization process, the final result of the ensuing rearrangement is that it is the most loosely bound electron that has been removed. This concept explains many of the subsequent bond fragmentations, if it is assumed that the driving force leading to fragmentation is the stability of the fragments formed, both charged and uncharged. Thus in ketones $RCOR_1$, the bond adjacent to the carbonyl group is known to break easily. This is the result of the removal during ionization of one of the loosely bound lone-pair electrons on the oxygen atom, and is explained by the stability of the $RC{\equiv}O^+$ ion formed at the same time as the radical $R_1\cdot$. Similarly,

$$R{-}\overset{\overset{O}{\|}}{C}{-}R_1 + e \rightarrow R{-}\overset{\overset{+\cdot\,O}{\|}}{C}{-}R_1 + 2e \rightarrow R{-}\overset{+}{C}{\equiv}O + R_1\cdot + 2e$$

aliphatic ketones with aliphatic chains more than three carbon atoms long can break the bond in the β-position relative to the carbonyl group, with simultaneous rearrangement of a hydrogen atom. This is explicable in terms of a series of electron shifts illustrated by the process for di-n-propyl ketone



This gives a product that is further stabilized by resonance. In this illustration, the convention used is that a

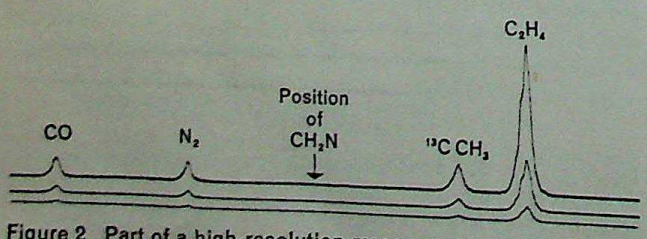


Figure 2 Part of a high-resolution mass spectrum, showing a multiplet at mass to charge ratio 28.

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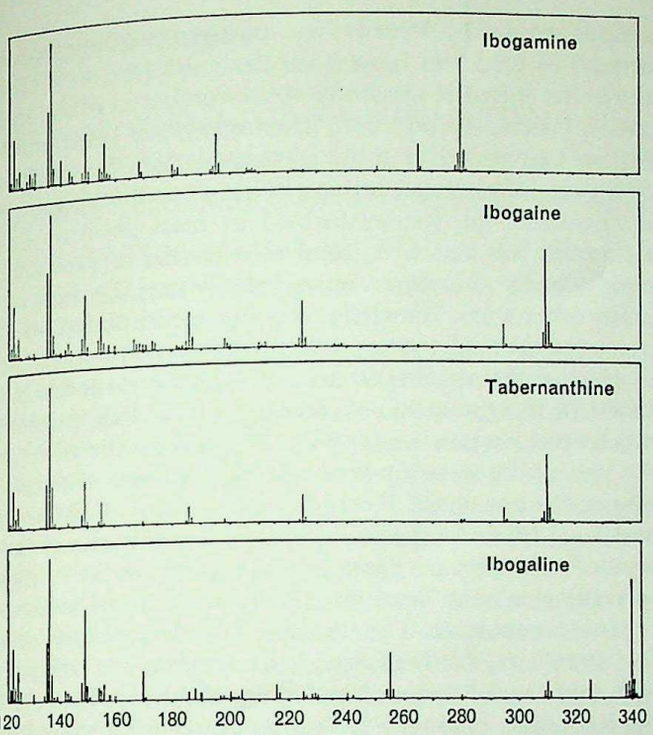
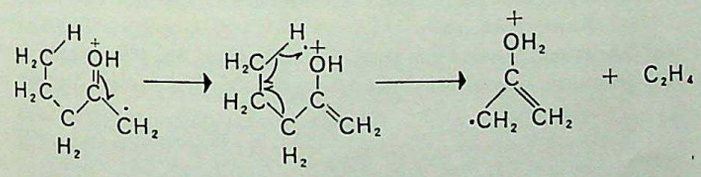


Figure 3 Mass spectra of four alkaloids from *Tabernanthe iboga*, all of which have different degrees of methoxylation.

'fish-hook' (⌒) represents the movement of a single electron [12, 13].

This fragmentation process, with rearrangement of a single hydrogen, yields a stable ion, together with a stable molecule as the neutral fragment. Indeed, if both alkyl chains are more than three carbon atoms long, a further decomposition with transfer of a second hydrogen atom can occur by the process illustrated below:



This example shows how familiar concepts, such as the ready formation of a six-membered ring, can be used to explain many of the features of complex spectra and to suggest the structures of the activated complexes formed as intermediates during the decomposition reactions. This work, which now has indicated plausible mechanisms by which many ions are formed, was pioneered by F. W. McLafferty [14] and has been systematically applied by C. Djerassi [13] to provide a rational explanation of the fragmentation patterns of a wide variety of types of compound. The approach has been reinforced by a great deal of work [15] using isotopic labelling to determine the source of the hydrogen and heavier atoms that may take part in rearrangements. By such methods, a detailed picture is being built up of the way in which the loss of an electron to form a molecular ion leads to charge redistribution throughout the ion, and controls the subsequent fragmentation pattern.

Applications

In the early mass spectrometers, it was difficult to insert the samples, but the difficulties have now largely been overcome, and the use of direct probe inserts makes it possible to examine fractions of a microgram of materials of molecular weights up to 3000 or 4000 on a routine basis [16]. Indeed, any organic molecule which can give a vapour pressure of 10^{-5} torr at a temperature below 500°C without decomposition can be investigated.

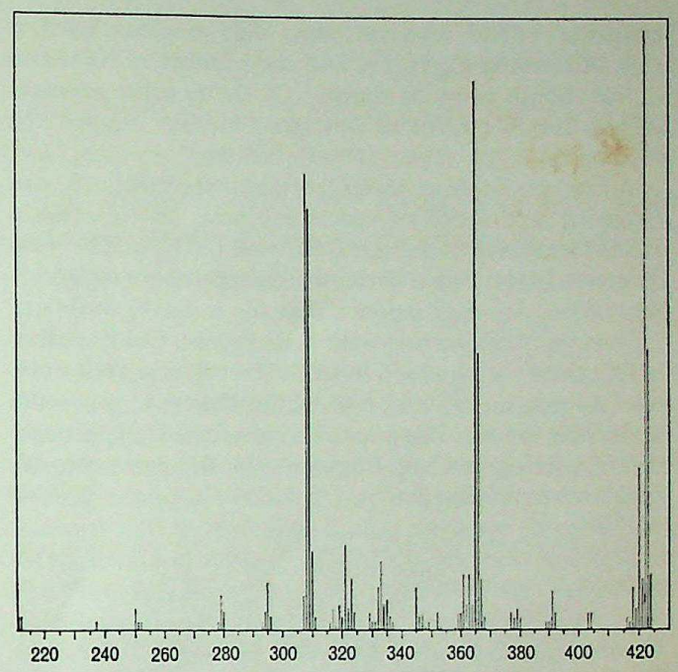
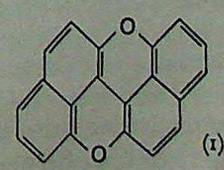
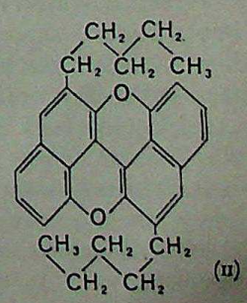


Figure 4 Partial mass spectrum of a fungal derivative.

Mass spectra complement the information available from other spectroscopic techniques, and the information provided is so precise and detailed that it is often chosen as the main technique to be used for examining a compound about which very little is known. It has proved especially valuable in the elucidation of the structures of natural products that are obtainable in only very limited amounts. A single example of its use will perhaps illustrate its power. The partial spectrum shown in figure 4 is that of a fungal derivative [17, 18]. The peak at mass 422 is assumed to be due to the molecular ion; its measured mass of 422·223 ± 0·004 u and the isotope peaks at masses 423 and 424, of relative abundance 32·62 per cent and 6·05 per cent of that of the peak at mass 422, fit only the formula $C_{30}H_{30}O_2$. A fully saturated molecule containing 30 carbon atoms and two oxygen atoms would contain 62 hydrogen atoms. Thus the formula $C_{30}H_{30}O_2$ indicates that the molecule contains rings and double bonds in numbers such that together they add up to sixteen. The major fragmentations to give peaks at masses 365 and 308 can be shown by accurate mass measurement to represent the loss of C_4H_9 and C_8H_{18} from the molecular ion. Empirical rules of fragmentation suggest that this indicates the presence of two n-amyl groups on an unsaturated nucleus; the side chains cannot be branched, because otherwise fragments corresponding to cleavage at the





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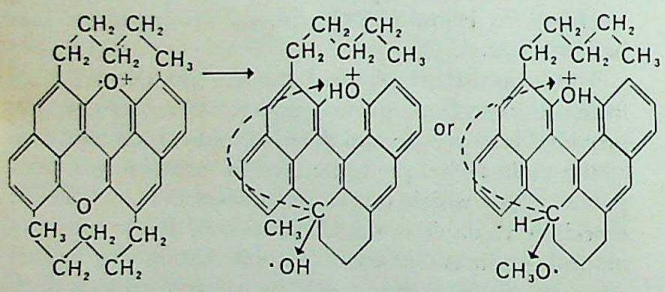
branches would also be seen. The nucleus itself is thus of formula $C_{20}H_{10}O_2$ and the number of rings and double bonds must be sixteen. Of the possible arrangements, the fragments of low mass number suggest the nucleus (I).

A sample of this material (perixanthenoxanthene) was obtained and its mass spectrum found to be characterized by loss of fragments CHO and $C_2H_2O_2$. The mass spectrum of the fungal derivative does not show such fragmentation, and this suggests that the n-amyl groups are in some way interacting with the oxygens. Confirmation of this theory is obtained from the fact that peaks can be seen at masses 279 and 250, indicating that when the molecular ion has fragmented to lose two C_4H_9 groups, the remaining nucleus fragments in the same way as perixanthenoxanthene:

$$422^+ \rightarrow 365^+ + 57\ (C_4H_9)$$
$$365^+ \rightarrow 308^+ + 57\ (C_4H_9)$$
$$308^+ \rightarrow 279 + 29\ (CHO)$$
$$279 \rightarrow 250 + 29\ (CHO)$$

From arguments of this kind the structure of the fungal derivative was deduced to be (II) and the importance of peaks at masses 403 and 391 can now be appreciated. They are caused by rearrangement fragmentations with elimination of OH and CH_3O:



There is also elimination of H_3O and CH_5O from the molecular ion, causing unsaturation in the new rings formed. This is merely a single example of the very large number of such deductions of molecular structure which are nowadays being carried out as a routine.

Recent improvements

Developments in instrumentation are still taking place. They aim at speeding up the process of plotting the mass spectrum, and at aiding the chemist in its interpretation. New equipment will make it possible to scan a spectrum containing several hundred mass peaks in less than a minute, and the pioneering work of K. Biemann [19] has suggested ways of using a computer to process the information in the mass spectrum. It can be presented in the form of an 'element map', in which the nominal masses of the ions are listed, with the elemental composition of the ion or ions responsible for the peak or peaks at this mass number recorded against each one. This work is still in its early stages, but it is already clear that it will reduce considerably the time taken to analyse a complex spectrum.

Mass spectrometry, once the province of the physicist, is now a subject in which the organic chemist is taking an increasing interest. There is, however, the exciting work concerned with such matters as lifetimes and stabilities of ions, and with the energetics of their formation. As physical chemists begin to explore these fields, instruments will undoubtedly be further developed to meet their specialized needs. Already new ion sources using photons instead of electrons have been designed [20, 21]: these are better suited to the study of the energetics of the ionization process. In addition, instruments are being modified so that they can study metastable ions better [22], and gain information on the lifetimes and stabilities of intermediate ion species formed in mass spectra; field ionization has also been used as a means of producing molecular ions having no excess energy [23]. In these and many other ways, knowledge is being accumulated on the processes that take place when organic compounds are ionized in the mass spectrometer. This knowledge will make the interpretation of spectra for analytical purposes much more certain, and it will also open up the whole of the new and accessible field of the chemistry of positive ions in the gas phase. Recent work by M. S. B. Munson and F. H. Field [24] has already shown that the ionization of mixtures of gases at high pressure in a mass spectrometer may lead to a new method of ionizing organic compounds. The resulting knowledge of the relative stabilities, lifetimes, and cross sections for collisions with other ions or neutral molecules of the ions formed in the ionization chamber has already suggested some new routes for the synthesis of organic compounds.

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The evolution of the cultivated potato

Kenneth S. Dodds

There are representations of the potato on pottery dating from the third century B.C., but there are no traces of the actual plant in the refuse of primitive peoples, and the course of its development is therefore unknown. This article describes what has been deduced about the origin and cultivation of the various strains in South America, and about the transmission of the plant to Europe. It also discusses the new varieties that may be developed by hybridization with wild strains.

'Floury roots of good flavour, a gift very acceptable to Indians and a dainty dish even for Spaniards.' This statement, translated from Spanish, concludes what is probably the first written description of the potato [1]. The author was one of a party of Spaniards who penetrated into the Andes in 1537 by way of the Magdalena Valley (see map) in Colombia, at that time part of the realm of the Incas. He was telling of the foodstuffs that were encountered in one of the villages on the high plateau. The potato, however, was a domestic plant long before the advent of the Incas, who arrived relatively late in the history of South America; and where, how, and by whom it was brought into cultivation will probably remain an unsolved mystery. Because of the absence of any form of writing to give a clue to dates, all the history of South America before the Spanish Conquest is shadowy; and, unlike corn, beans, groundnut, squashes, and pumpkins, for example, traces of the potato have not been preserved in the occupation refuse of primitive peoples to tell an evolutionary story. The little that is known about its origin has had to be deduced mainly from information about the geographical distribution of the crop in the world today and from studies of the cytology and genetics both of the cultivars—the cultivated plants—and of related wild species.

The potato definitely originated in South America, for it was not known either in the Old World or in North and Middle America before the Spanish Conquest. Its original home is in the Andes, from North Argentina to Venezuela, where it shows a diversity that is related to the ecological diversity of this vast region—a region which embraces high mountain ranges, valleys, intermontane basins, and high plains known as puna or altiplano. The greatest local variability of the crop is to be found on the altiplano around Lake Titicaca, where a high proportion of the Indian population of South Peru and Bolivia is concentrated and practises a subsistence type of agriculture that has changed little since Inca times (figure 1). Nowadays, however, barley, beans and a few other crop plants from the Old World are grown, in addition to indigenous ones such as maize (*Zea mays* L.), quinoa (*Chenopodium quinoa* Willd.), oca (*Oxalis tuberosa* Molina), ulluco (*Ullucus tuberosum* Caldas), añu (*Tropaeolum tuberosum* Ruiz & Pav.), and potatoes, which were the mainstay of agriculture before the Spanish Conquest.

Kenneth S. Dodds, *D.Sc., Ph.D.*
Was born in 1912 and educated at Durham University. In 1937 he joined the staff of the Imperial College of Tropical Agriculture, Trinidad, West Indies, to work on the cytogenetics of bananas. He was Professor of Botany there from 1947 to 1949, when he left to become Director of the Potato Genetics Station, Cambridge. In 1954 he was appointed Director of the John Innes Institute, the potato unit moving with him. He has recently accepted an appointment with the Food and Agriculture Organization of the United Nations to study vegetables and fruits in Turkey.

Early history

The earliest records of the potato in South America are the representations of it on pottery that occur in the Mochica culture, which is thought to have existed for several centuries before it was obliterated in the third century A.D. by the spread of a highland culture. The Mochica culture was established in the northern half of the Peruvian littoral, but the possibility that the potato was domesticated in this warm coastal zone can be discounted. It requires a temperate climate in order to thrive, a climate such as that which, in the tropical and subtropical latitudes of South America, is to be found only high in the Andes. The earliest known culture on the altiplano is the Tiahuanaco, which dates back as far as about 200 B.C. It is named after the place on the Bolivian plateau to the south of Lake Titicaca, where there are ruins of what is believed to have been a ceremonial centre. However, the potato must have been domesticated long before the Tiahuanaco culture.

Virtually nothing is yet known about still earlier inhabitants of the altiplano. Early man is assumed to have

Map of South America.

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Figure 1 Potatoes on the altiplano near Lake Titicaca.

reached South America by way of the Isthmus of Panama and then to have followed the Cauca or Magdalena Valley into the Colombian highlands and so southwards along the Andes, moving in a region relatively free from dense forests but with a plentiful supply of animals for hunting. Traces of early man dated about 7500 B.C. have been found in cave deposits at Laurichocha near the source of the River Marañón in the Central Peruvian Highlands, at a height of over 13 000 ft. Leaf-shaped points from primitive tools in the second horizon of these deposits closely resemble some from a deposit dated about 6000 B.C. at Ayampitín, Argentina [5]. Whether these early hunters themselves invented agriculture on the altiplano or were replaced by a migratory people who brought agriculture with them is an open question.

Chromosome situation

The chromosome numbers of the indigenous cultivated potatoes of South America form a series consisting of diploids—plants with two basic sets of chromosomes—and triploids, tetraploids, and pentaploids with three, four, and five sets respectively (figure 2).

The origins of the higher chromosome numbers in potatoes are not known with any certainty, but cytological evidence suggests that all the chromosome sets of the majority of triploids, and of all the tetraploids, are essentially similar to the basic set of the cultivated diploids, this being the primitive set. The potato is propagated either vegetatively, by the tubers, or sexually, by true seeds, and during sexual reproduction in a diploid, the 24 chromosomes pair in 12 bivalents and then separate to give 12 chromosomes at opposite poles of the cell (figure 2). The cell divides, and after further divisions, reproductive cells are formed with the reduced haploid number of chromosomes (12). These are called gametes. Sometimes chromosomes do not separate and rare gametes are formed with the unreduced chromosome number (24). The union of a reduced and an unreduced gamete would give a cell capable of developing into an individual with the triploid chromosome number (36), and if two unreduced gametes fused, the individual would be tetraploid. The probability of either of these events occurring is extremely low, but on balance the probability of the first type of behaviour is higher than that of the second. Thus, in the beginning, triploids may well have been more numerous than tetraploids. This situation would not last very long, however, because triploid potatoes have a very low fertility, whereas most tetraploids are fairly fertile. Once established, tetraploids would be a source of unreduced gametes containing 24 chromosomes, and, by self-fertilization and by crossing with diploids and with other tetraploids, they would tend to augment the number of polyploids, with every probability that, in the progeny, tetraploids would predominate.

The problem of classifying this material has posed nomenclatural problems. Taxonomists have offered many—too many—Latin binomials for the different groups, some of which are based on no more than a single clone—a group of plants propagated vegetatively from a single individual—or a small group of clones. Cytological investigations, however, show that with the exception of two small groups of hybrid triploids and pentaploids referred to below, all cultivated potatoes, no matter how diverse morphologically, share a common origin and a common genetic system. There is no justification for the recognition of 'species', and in the circumstances it seems preferable to use only one Latin binomial, *Solanum tuberosum* L., as the collective name for the whole assemblage, and then to subdivide by ploidy and agronomic characters [2].

Cultivation

Some diploid potatoes at the northern end of the distribution range (that is in Venezuela, Colombia, Ecuador, and Northern Peru) are locally called '*papa chauca*'. In marked contrast to the diploids grown on the altiplano, which give tubers that remain dormant during the winter months and so can be stored until the next planting season, those of '*papa chauca*' begin to sprout soon after harvest. In suitable frost-free areas they can be replanted at once, and can give two or even three crops annually. They are highly valued ingredients of soups and stews, and a specialized trade has developed to meet the demand for them, especially near to Lima and Bogotá.

On the altiplano in Southern Peru and Bolivia, diploids, triploids, and tetraploids, and, less frequently, pentaploids, are indiscriminately mixed in both field and market. Some idea of the extent to which this might occur is given by chromosome counts made by C. Ochoa [3] of a sample of potato varieties collected in the region around Lake Titicaca. Of a total of 465 different

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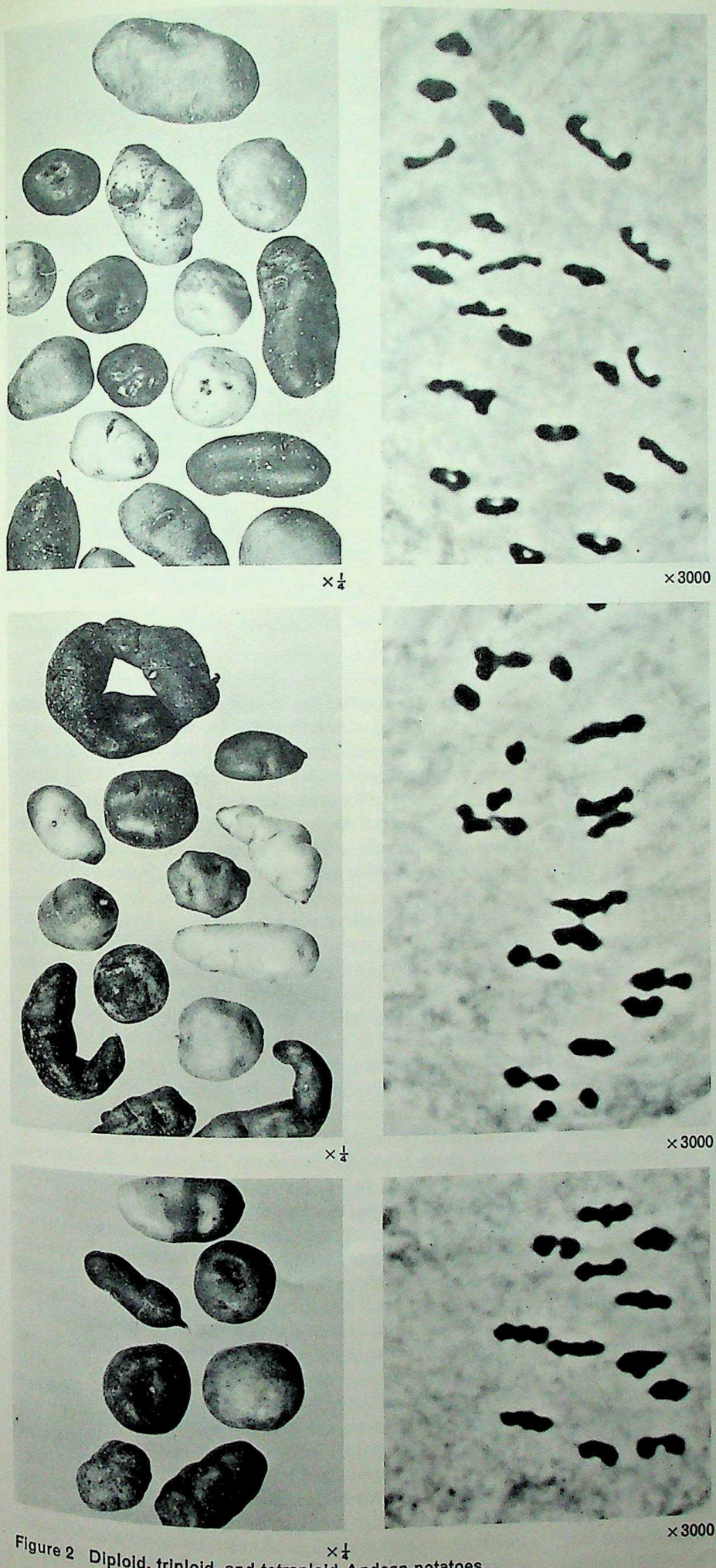

Figure 2 Diploid, triploid, and tetraploid Andean potatoes.

varieties, 159 were diploids, 111 were triploids, 170 were tetraploids, and 19 were pentaploids. Precise comparative trials of the yields of diploids, triploids, and tetraploids have not been made on the altiplano, but general observations suggest that, on average, tetraploids and triploids outyield diploids. Presumably this superiority in yield is the selective advantage which has led to the adoption of polyploids. On the most progressive farms in the Andean valleys, the commercial production of potatoes is based entirely on tetraploids; but, as we shall see later, tetraploid selection has been taken even further in the north temperate countries to which the potato has been introduced.

Very gradually the farming methods of the Indians on the altiplano are being improved, and so it is inevitable that eventually they will be encouraged to discard their mixed stocks of potatoes and to use instead better-yielding tetraploids—as farmers elsewhere in the Andes are doing. In an effort to combat the 'gene-erosion' which this change entails, extensive potato collections have been made to serve as 'germ plasm banks' for the preservation of genetic variability.

Sometimes pentaploids and a distinct class of triploids are grown on the altiplano in plantings separate from the general run of potatoes. Among the 111 triploids examined by Ochoa, 49 belonged to this class, and there were 19 pentaploids in the total sample of 465 varieties. Members of both classes are frost-resistant, like the wild tetraploid species *Solanum acaule* Bitt., which is a native of the altiplano and higher mountain ranges; and they also resemble this species in several morphological characters. Thus it seems extremely probable that the special triploids, subsumed under the name *S.* × *juzepczukii* Buk., originated by hybridization between one or more cultivated diploids and *S. acaule;* and that the pentaploids, subsumed under the name *S.* × *curtilobum* Juz. et Buk., were formed by the union of unreduced triploid gametes from *S.* × *juzepczukii* with normal diploid gametes from cultivated tetraploids. These ideas have been confirmed by J. G. Hawkes [4], who synthesized the hybrids and showed that they are very similar, both morphologically and cytologically, to the naturally occurring plants. The hybrid

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triploids and pentaploids are used to make *chuño*, a dehydrated product that can be stored indefinitely. It is obtained by allowing the potatoes to freeze during the night and treading them next day: after four or five consecutive days of such treatment, they are dried in the sun. Ordinary *chuño* is grey, but a white *chuño* is obtained by steeping the trodden potatoes in water for one or two months before drying. *Chuño* was probably the basic 'marching ration' of the high Andes.

Wild relatives

The genus *Solanum* L. is extremely large, containing over 2000 species, and of these more than 100 are tuber-bearing (figure 3). As in the cultivars, the chromosome numbers of the wild tuber-bearing species form a polyploid series. However, in this case the series extends from diploidy to hexaploidy. These wild relatives of the potato are distributed more or less continuously from Colorado to Chile and Argentina, and they are as variable in habit as they are in habitat. Several species occur in the high Andes of Bolivia and Southern Peru; examples are the diploids *S. sparsipilum* and *S. leptophyes*, both of which are probably allied to the cultivated plants. Nevertheless, the facts do not permit either one of these species, or for that matter any other, to be regarded as the wild ancestral species of the potato. Indeed, it is quite possible that the ancestral species was entirely domesticated and disappeared long ago. All that can be said at the present time is that there are several species of the potato that might have been the original subject for domestication.

The altiplano is a large inland basin that sits figuratively on the roof of South America at an average altitude of about 13 000 ft. To the west, the sparsely populated western Cordillera is the watershed between the Pacific and the altiplano, while to the east, the eastern Cordillera is a barrier between the altiplano and the tropical lowlands. The north-eastern section of the eastern Cordillera drops precipitously to the Yungas (Amazonian forest), but in the southern section the descent to the tropical lowlands is more gradual.

These slopes are dissected by long valleys in which large basins provide favourable areas for cultivation and settlement at altitudes between about 8 000 and 10 000 ft. The most northerly valley, the one in which Cochabamba is sited, drains into the Amazon, but the others, the valleys which contain Sucre and Tarija in Bolivia and Jujuy, Salta, and Tucumán in north-western Argentina, drain ultimately into the Rio de la Plata. If the first farmers on the altiplano came from elsewhere, did they reach it by way of the valleys which lead up from what is now north-western Argentina? And did they carry the potato with them? The supposition that migration from the east over the Andes did occur quite early in the history of South American agriculture is supported by the observation that traces of groundnut, a plant which originated east of the Andes, probably in north-western Argentina, occur in archaeological sites on the Peruvian coast at levels more or less contemporaneous with the appearance of pottery estimated at about 1000 B.C. [6]. Furthermore, several wild species fairly closely related to the potato are native in north-western Argentina.

As a working hypothesis, it may be supposed that the diploid cultivars originated from diploid wild species

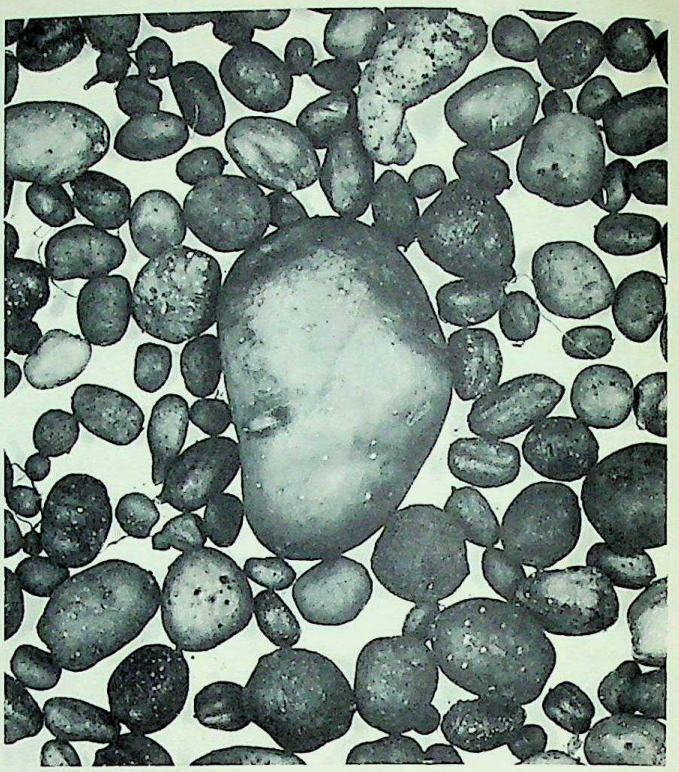

Figure 3 Tubers from wild species compared with a King Edward tuber. ($\times \frac{1}{2}$)

occurring as weeds in maize cultivated at middle altitudes—up to about 10 000 ft, above which maize disappears. The very limited field observations that were made to test this idea have not given a decision either way. The potato weeds in the maize fields around Cochabamba and near to southern Peru appear to be either distinctively wild plants, or escaped cultivars that have run wild. More extensive field work is needed.

The potato in Europe

In dealing with South America it is the history of the potato prior to the Spanish Conquest that is of primary interest, but in Europe the situation is reversed. The European history of the potato is fairly well chronicled in a general sort of way, but the precise dates when the first introductions were made, how they were made, and whence in South America the potatoes came, are not known.

The earliest known reference to potatoes in Europe occurs in account books of the *Hospital de la Sangre* in Seville, Spain, in which purchases of potatoes are mentioned in 1573. As the potato was not recorded elsewhere in Europe at this time, this record suggests very strongly that it was introduced first into Spain; if a few years are allowed for getting plants established, the nearest estimate of the date of introduction is 1570.

At a somewhat later date, potatoes were also introduced into Ireland directly from the New World, and it was in reference to this material that the English herbalist Gerard listed the potato in his *Catalogus Arborum* of 1596. There is no evidence to support the legend that Raleigh was responsible for the introduction, although it does not seem unlikely that the potatoes came from the provisions of an English privateer. In so far as the tubers could be left in the ground until wanted, the potato was particularly well suited as a crop for Ireland under the unsettled farming conditions that prevailed during the

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sixteenth and seventeenth centuries, and it was adopted quickly. By the nineteenth century, as is well known, its use was so widespread that when the crop failed in 1840 owing to an epidemic of Late Blight, national famine ensued. The potato spread to Scotland and England from Ireland. Starting from Spain, the spread of the potato in Europe was similar to that in England, inasmuch as social changes helped to overcome objections to the crop and to foster its acceptance. The potato was probably taken to North America in 1719 by Scottish or Irish immigrants who established a colony at Londonderry, New Hampshire.

Because a small group of varieties collected in Chiloé (an island off the coast of Chile), at about latitude 42°S, proved to be tolerant of long days and not unlike European potatoes in some other respects, Russian botanists have contended that the potato was introduced into Europe from Chiloé or the nearby mainland. Historical evidence alone weighs heavily against this hypothesis, and furthermore it is known that Andean potatoes have the genetic potentiality to respond readily to selection for tolerance of long days. Thus it is now generally accepted that the potatoes originally introduced into Europe came from the northern Andes and have since then been considerably changed by selection.

All the original and intermittent later introductions of the potato into Europe were tetraploids; presumably, like their present-day counterparts in the Andes, they were reasonably fertile and bore a number of alternative genetic factors. Thus they would give very variable progeny. There were only a few different varieties at first, owing to the very limited scale of introduction, and it was not until seedlings were raised in quantity that any marked increase can have occurred. The exact date when this began is not known but they were widely raised from the end of the eighteenth century onwards, with a consequent rapid increase in the number of varieties. Breeding methods were empirical, and they remained so until the end of the first quarter of the present century, when developments in cytology and genetics opened up the possibility of a more scientific approach.

In the Andes, potatoes are adapted to about 12 hours of daylight, and when grown under a daylength of about 16 hours, such as prevails during the summer in Europe, they tuber poorly or not at all (figure 4). They also mature late and are extremely susceptible to Late Blight. They commonly produce irregularly shaped, pigmented, deep-eyed tubers (figure 5) borne on long stolons (underground stems), and on average they have more foliage and smaller leaflets than European potatoes. One of the first responses to selection in a European environment was tolerance of long days. Another early change was in time of maturity; even before the end of the eighteenth century, a distinction was being made in Ireland between main crop and early varieties. Since then the time taken to reach maturity has been reduced progressively, until nowadays even main crop potatoes are harvested well before the beginning of autumn; and they carry their large, regularly shaped, and smooth tubers on relatively short stolons. This evolutionary path is being retraced by N. W. Simmonds [7] in a long-term experiment which has as its aim the re-creation of the European potato from Andean stocks. Under a form of semi-natural selection

Figure 4 An Andean potato fails to develop tubers when grown under long days.

obtained by a combination of mass selection and pedigree methods, the third generation progeny already shows earlier and heavier cropping, owing to an improved tolerance of long days. Changes in the direction of the European potato are being obtained in characters which are part of the daylength syndrome, such as amount of haulm, earliness of tubering, and length of stolon; but not in others which are independent of it, such as leaflet size and tuber shape, size, and colour. The inference is that the latter group of characters was changed mainly by conscious human selection. So far, the results give reasonable grounds for confidence that the entire pathway from the Andean to the European potato can be retraced experimentally.

Future developments

The long evolutionary history of the potato has culminated in the highly adapted European and North American varieties. At first glance, it would seem to be possible to produce further radical evolutionary divergence by the use of modern breeding methods, by which desirable characteristics from wild species can be incorporated on a scale and at a rate that would be quite impossible in nature. However, the small, inedible tubers of wild species are as closely adapted for natural survival as the large, edible tubers of cultivars are for human needs. Each type is the product of a highly specialized

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Figure 5 Andean potatoes (left) compared with King Edwards (right). (×½)

physio-logical system and the two systems cannot be expected to complement one another in a hybrid, at least in attributes such as yield and quality. Indeed, the strict varietal standards that must be met in characters such as yield, maturity period, and general consumer acceptance will themselves ensure that the gains of past selection are not jeopardized by indiscriminate hybridization. With this in mind, it may be suggested that the value of wild species will be mainly confined to their use as sources of genes conferring resistance, for incorporation in the varieties of the future. Some useful characters which have been found are the following: immunity to virus *X* and frost resistance in *S. acaule* Bitt.; immunity to virus *Y* and *A* in *S. stoloniferum* Schlechtd. et Bche. and *S. chacoense* Bitt.; field resistance to Late Blight in *S. demissum* Lindl. and *S. stoloniferum;* resistance to races of Potato Root Eelworm in *S. spegazzinii* Bitt. and *S. vernei* Bitt. et Wittm.

The use of the Mexican hexaploid species *S. demissum* for Late Blight resistance is a familar story in the annals of potato breeding. Its sequel—the ease with which resistance can be overcome by newly adapted strains of the fungus—has become an equally familiar story in the general annals of breeding for resistance. Breeding with this species began with resistance that is controlled by a few major genes, referred to as *R*-genes: they induce a hypersensitive reaction in the host which has the effect of confining the initial points of fungal infection within lesions. But nowadays interest has switched, as with many other fungal diseases, to 'field resistance'. This is governed by a large number of genes, each with a small effect. It is assumed that this multigenic control will considerably reduce the probability of appropriate mutations occurring in the parasite to give strains capable of infecting the resistant host.

If, as suggested, the value of wild species to potato breeding is limited to their use as sources of genes for resistance, the problem remains of where to seek future advances in the yield and quality of potatoes. There is reason to believe that they may come from hybrids between Andean and European cultivars which are known often to give productive progeny. Whether these seedlings owe their good performance to specific gene interactions, or whether they merely represent the exploitation of hitherto untapped genetic variability, are problems for future investigation.

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Nuclear microscopy

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G. R. Bishop

The nucleus of the atom is usually regarded as a dense central mass occupying only about 2 parts in 10^{14} of the atom. This value is derived from Rutherford's observations of the anomalous scattering of a stream of α-particles. For a number of reasons, electrons are more suitable probes than α-particles, and this article describes experiments using electron probes, and the results obtained from them, which include the discovery that many nuclei are ellipsoidal.

More than half a century ago, in 1911, Rutherford published the first of his mathematical papers seeking to explain the reason for the occasional large deflections that were observed when positively-charged α-particles passed through air, mica, or gold. Two years later Bohr produced his successful theory of the origin of atomic spectra and essentially completed the Rutherford-Bohr model of the atom that we teach in our schools today. The Rutherford-Bohr model associates all the positive charge of the atom, and most of its mass, with a small central nucleus that has electrons moving in orbits at distances of about 10^3–10^4 times the nuclear radius. Rutherford's theory of α-particle scattering was generalized by Darwin, who worked out the solutions of the classical mechanics problem where the force between particles varies as the inverse nth power of their separation. In 1920, Chadwick showed experimentally that $n=2$ for the scattering of α-particles by heavy nuclei, and therefore that Coulomb's law—the inverse square law—is valid for these collisions. Just previously, Rutherford had shown that deviations from the scattering which would be produced by a pure Coulomb field are experimentally evident when α-particles are scattered by the lightest elements. The distance of closest approach at which this anomalous scattering occurs was taken as the first measure of the nuclear radius. A value of 5 fermis (1 fermi = 10^{-13} cm) was deduced from these experiments; the radius of an atom is about 10^{-8} cm.

To emphasize how remote from everyday experience are the consequences of this model, it is worth calculating that the nuclei occupy only about 2 parts in 10^{14} of the volume of solid material, and that the density of nuclear matter is then of the order of 10^{14} grams per cm^3. This article describes one of the modern methods employed to study the spatial structure of nuclear systems.

Our present concept of nuclei, based on a wide variety of experimental evidence, is that they are composed solely of neutrons and protons—nucleons—which are bound together by strong short-range forces. The shape of the nucleus is usually substantially spherical—some are ellipsoidal, as we shall see—because for a given volume this shape possesses the least surface area and leads to maximum effectiveness of the short-range internucleon binding forces. The nuclear volume is proportional to the number of nucleons in a given nucleus, which means that nuclear matter is essentially incompressible and has a constant density for all nuclei. While the nuclear surface cannot be delimited as accurately as that of a billiard ball, for example, there does exist a surface outside of which there is a negligible probability of finding any of the nuclear constituents. Accurate measurements of the radius of this surface involve the interaction of the nucleus with probe particles, which may be nucleons themselves, or simple nuclei such as α-particles, or electrons, mesons, or other elementary particles. The use of each type of probe leads to a specific definition of the nuclear radius, since the detailed nature of the forces enters into the interpretation of experiments, and for most of them this is imperfectly known. Despite this vagueness, the radius can be specified to within less than one fermi—an imprecision of about 10 per cent. We understand electromagnetic forces much better than nuclear forces, however, so that probes such as the electron and the μ-meson, which interact with nuclear matter through their electric charge, lead to values for the electromagnetic radii with uncertainties of only one per cent. From the electromagnetic potentials of the nucleus as determined by electron or μ-meson scattering, we can arrive at the charge and magnetic moment distributions in the nucleus by means of Maxwell's equations. By using nucleon probes alone, we learn something about the nuclear potential between the nucleus and the probe, but in general we cannot deduce anything about the nuclear density distribution from the potential, since we do not know the nuclear equivalent to Maxwell's equations. The electromagnetic probe has the advantage that, during the measuring interaction, it causes only minor perturbations to the nucleon motions inside the nucleus, which are determined principally by the strong internucleon forces.

George R. Bishop, *M.A., D.Phil., F.R.S.E.*
Born in London in 1927 and educated at Alleyns School, Dulwich, and Christ Church, Oxford. After research at the Clarendon Laboratory, Oxford, until 1955, he joined the *Ecole Normale Supérieure*, Paris, where he remained until his appointment to the Kelvin Chair in the University of Glasgow in 1964. He was appointed *Professeur Associé à la Faculté des Sciences d'Orsay* in 1962, where he was responsible for the experimental programme executed with the 1·3 GeV electron linear accelerator.

Experimental apparatus

The use of electrons to investigate nuclear sizes and shapes involves experimental apparatus of which the elements can be described in a useful analogy with the parts of the familiar electron microscope. An electron nuclear scattering experiment uses an accelerator of electrons, a focusing device to produce the correct energy and angular definition of the electron beam on the sample, and a detector to register the scattered electrons. These elements are rather different in detail, however, from those in the electron microscope, as might well be expected, in view of the range of 10^5 to 1 in the size of the objects to be studied.

To obtain anomalous nuclear scattering of electrons it is necessary that the de Broglie wavelength of the electrons should be comparable to the size of the nucleus. An electron with an energy of 197 MeV has a de Broglie wavelength of 1 fermi. Such electrons are highly relativistic, that is, their rest mass, of only 0·51 MeV, can usually be neglected in comparison with their kinetic

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energy. What sort of accelerator will impart a kinetic energy of a few hundred MeV to an electron? This energy cannot be obtained by simply allowing the electron to cross a static potential difference of 200 MV, because we cannot generate such a large potential drop. Instead, a choice is made between two eminently realizable accelerators employing different principles. The first principle is that of causing the charged particle to traverse an easily generated small potential drop a large number of times, in such a way that the successive accelerations accumulate until the particle's kinetic energy has the desired value. In between successive accelerations, the particle trajectories are constrained to the dimensions of the accelerator by static or dynamic magnetic fields. Such accelerators are called cyclic accelerators and are by far the most numerous in the world's laboratories. The second principle is to arrange that the charged particle be subjected to an electric field which is generated in such a fashion that it moves in strict synchronization with the particle. The particle, in consequence, is accelerated by a force equal to the product of its charge and the amplitude of the synchronized electric field over the whole length of the accelerator in which the field is maintained. Such an accelerator is most conveniently disposed along a straight line and is called a linear accelerator. Since the gain in particle energy per unit length of linear accelerator is limited by the problems of generating the electric field, the maximum final energy is proportional to the length of the accelerator. The longest linear accelerator of electrons is due to operate at Stanford, California, in 1966 and over a length of 10 000 feet will raise the energy to 20 GeV.

As the electron is relativistic, it traverses the length of the linear accelerator with practically the velocity of light, in times of the order of a microsecond. The electric field, in the form of a wave, must travel at the same velocity to keep pace with the electron. The electron can be pictured as riding the crest of the wave or, in other words, moving at a definite phase with respect to the wave. In the cylindrical copper guides used to contain such electromagnetic waves, the phase velocity normally exceeds the velocity of light. To obtain synchronization between the wave and the electron, whose velocity cannot exceed that of light, the wave is slowed down by loading the guide with copper irises. The iris blocks off the guide into a succession of cavities; a central hole in each iris lets through the electron beam and the electromagnetic wave (figure 1). Energy for the wave is supplied by radio-frequency sources spaced along the length of the accelerator. These sources are magnetrons or more often klystrons, widely known for their use in radar installations. To establish electric waves with amplitudes of about 100 kV per centimetre in the guide, a power level of 25 megawatts is required of the klystron. Such large powers can be maintained for pulses of only a few microseconds duration, followed by intervals of a few milliseconds to allow for adequate cooling of the klystron and guide. The product of pulse duration and repetition rate is called the duty-cycle of the accelerator and for existing linear accelerators it is small, less than 10^{-3}. Short duty-cycles complicate seriously the experiments performed with an accelerator, since the information required of it must be recorded during the pulse itself, when some 10^{12} electrons are striking the target. In particular, the recording of coincidence events between two radiations leaving

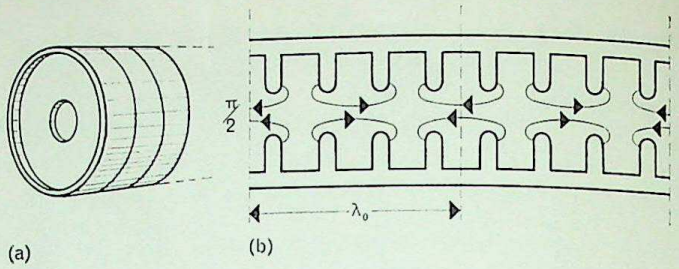

Figure 1 (a) Waveguide with iris loading. (b) Travelling-wave electric field configuration for a commonly adopted mode of oscillation in which the phase shift per cavity is $\pi/2$. This wave travels in synchronism with electrons moving on the axis of the guide.

the target which are time-correlated because of a common nuclear interaction is next to impossible with an accelerator having a short duty-cycle.

A high vacuum is maintained in the accelerator waveguide to prevent sparking that could be caused by the large electric fields, and to avoid scattering of the electrons. At the end of the machine, the accelerated electrons easily penetrate the metal window holding the vacuum and issue as a pulsed beam. The electrons in a pulse do not all have precisely the same energy, since a range of phase values relative to the electric wave is consistent with acceleration throughout the length of the machine. A spread of one to two per cent in energy is commonly obtained, which is too large for high precision experiments demanding a spread of only one tenth per cent. The sorting out of the electrons according to their energy is accomplished by the focusing device. This is a system of 'bending' and 'quadrupole' electromagnets. The bending magnets act as prisms and disperse the electron beam spatially, thus displaying the spectrum of electron energies; the required beam is selected from the spectrum by a metal slit. The quadrupole magnets act as lenses, correcting the spatial extent and angular divergence of the selected beam and focusing it on the target sample. The radius of curvature chosen for the bending magnets is proportional to the electron energy, but for a given energy cannot be made smaller than a value determined by the saturation of magnetization of the iron yokes. The focusing device for electrons of a few hundred MeV therefore necessarily includes magnets weighing several tons laid out over distances of from tens to hundreds of yards.

Targets to be studied are usually in the form of flat thin plates of a suitable material. As far as possible the nuclear isotope, enriched to close to 100 per cent and in its elemental state is used, since all nuclei, including those foreign to the experiment, contribute to the scattering of electrons. The sample is usually held in a target chamber under a vacuum continuous with that of the accelerator and focusing device. The incident electron beam traverses the target and finally leaves the vacuum through a metallic exit window. Measurement of the incident beam current, a necessary datum in the experiments, is accomplished in various ways. Ideally the measurement should not disturb the beam itself, but this is difficult to achieve with the required precision of 0·25 per cent. Since the beam is charged and pulsed, it can induce charges and currents in conductors placed nearby. Thus if the beam is passed through a toroid of ferrite, the induced magnetization of the ferrite can be detected by the voltage it in turn induces in an auxiliary

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coil. This is a straightforward transformer action where the beam replaces the primary coil. The induced voltages are small, however, and their measurement in a building that contains several 25 megawatt pulsed radio-frequency sources is, to say the least, delicate. The current is measured extremely accurately by another method, that of the Faraday cup, in which the incident beam is arrested in an insulated cup and the accumulated charge is measured. To stop 500 MeV electrons, however, requires a block of lead weighing several tons. This is necessary because the incident electrons are brought to rest by converting their kinetic energy into heat energy of the stopping material, through a complex succession of competing processes called an electromagnetic cascade shower. Contributing processes are the radiation of *bremsstrahlung* photons, the production of electron-positron pairs, and the ionization energy loss of both electrons and positrons. Since the number of charged particles in a cascade shower initiated by a single incident electron may be very large at some stage of its development, the Faraday cup has to be large enough to prevent their escape. Similarly it must not collect charges produced by ionization of the air, so it is kept inside a vacuum envelope. The resulting equipment is a far cry technically from the Faraday cup of the ice pail experiment, but the principle is the same.

The electrons that are scattered by nuclei in the target contain the information of the experiment. They are very few in number compared either with the incident electrons or with the secondary particles, especially neutrons, that are produced by the incident beam. They constitute about 1 part in 10^9 of all the particles present in the experimental room during the microsecond flash of the beam delivered by the accelerator. Their selection and detection is performed in a sequence of operations, each of which has strong discriminatory powers against the irrelevant particles contributing to the background of the experiment. Most of the electrons traversing the target are deflected by less than one degree during scattering processes associated with the atom as a whole. Those electrons deflected through a larger scattering angle than one degree have necessarily suffered a close collision with a nucleus, 'seeing' its Coulomb field unscreened by the electron charges of the Rutherford-Bohr atom. Usually some form of magnetic spectrometer is adopted to detect the electrons scattered at large angles from the target. The function of the spectrometer is to collect electrons scattered in a small, well-defined angular cone about the desired scattering angle, transport them to the detector, and display their energy spectrum. These are much the same functions of focusing and dispersing performed by the focusing device of an electron microscope, but the initial conditions are very different, as is the purpose of the instrument. The geometry usually adopted for the spectrometer is that pioneered by Robert Hofstadter, which he adapted from β-ray spectroscopy. A flat semicircular magnet is used, set up in a vertical plane (figure 2), so that the analysed electrons are curled away from the target and detected at a distance from it. This geometry has the advantage of putting enough space between the target (the source of background neutrons) and the detector to allow considerable quantities of shielding materials to be inserted. The largest spectrometers of this type, currently in use at Orsay and Stanford, have radii of curvature of 2 metres

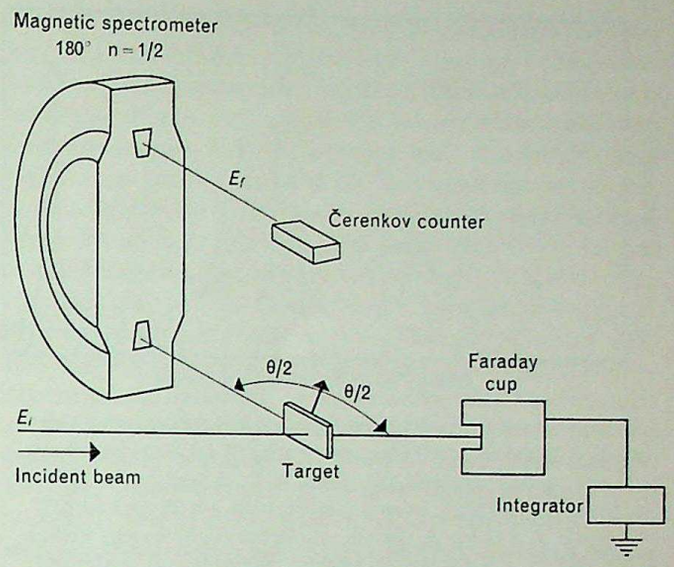

Figure 2 Diagram of the experimental apparatus used for an experiment on electron scattering by nuclei. The heavy arrow on the target indicates that the normal to the target plane is set to bisect the scattering angle θ.

and weigh several hundred tons. Great precision in manufacture is essential so that the magnetic field has the correct shape to give the required dispersion and focusing. Electrons of different energies leave the spectrometer at different distances from its optical axis, and this distance can be measured accurately and is related simply to the precise energy of the electron. The trajectory of the analysed electron is determined by its passage through a a geometrical arrangement of counters. The type of counter is again designed to discriminate heavily in favour of the electrons against background radiations such as neutrons. The physical principle of these counters is the emission of Čerenkov radiation by the relativistic electron when it traverses transparent materials such as Lucite. In large installations, the detector may furnish information simultaneously in a hundred or more channels defined by the counters and the magnetic field configuration. The treatment of these data is achieved by a programmed computer, which is capable of dealing more easily with the conditions imposed by the short duty-cycle than is the human experimenter.

Analysis of experiments

The raw data of an experiment made with the above apparatus consist of a series of energy spectra of scattered electrons determined by the spectrometer, for a chosen combination of incident electron energy E_i (determined by the focusing device) and scattering angle θ (angle between incident beam direction and the optical axis of the spectrometer). By energy spectrum is meant a plot of the number of scattered electrons, per unit of incident charge, as a function of their final energy E_f. A typical scattered spectrum (figure 3) shows a series of maxima or peaks separated by energy intervals which are characteristic of the sample material. Relative magnitudes of these peaks are found to depend on the values of E_i and θ, which can be varied at will with the apparatus described above. The interpretation of these peaks is reminiscent of the well-known Franck and Hertz experiments on the excitation of atomic levels by electrons. The scattered peak at the largest value of E_f corresponds to elastic scattering of the electrons by the nucleus which, after

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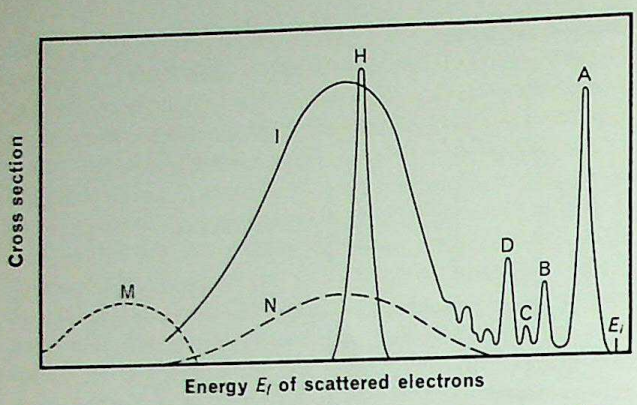

Figure 3 The spectrum of electrons inelastically scattered by nuclei. E_i is the incident electron energy. A is the elastic peak, followed by discrete inelastic peaks B, C, D, and so on. H is the free proton elastic peak observed from a hydrogen target; it appears at a lower E_f than A, since the recoil energy loss is much larger for hydrogen. N shows the incoherent scattering peak of an individual proton or neutron in the nucleus: it is broadened relative to H by motion within the nucleus. I is the simple sum of such N peaks for all the A nucleons in the nucleus. M represents electrons that during scattering produce π-mesons. The figure is not to scale.

the scattering, remains in the same internal state of motion. A small difference in energy $(E_i - E_{f\ max})$ is easily related by kinematics to the recoil kinetic energy of the nucleus in this two-body collision. Peaks at smaller values of E_f correspond to inelastic scattering of the electrons by nuclei which after the collision are in a new state of internal motion. The amount of energy transferred to the nucleus in an inelastic collision depends on the nucleus and the quantized energy-levels which characterize it. An enduring virtue of this method of exciting nuclear levels is that combinations of the experimental variables E_i and θ can be found to suit almost all nuclear levels connected to the ground state by simple adaptations of the motions of the constituent neutrons and protons.

Based on this general interpretation of the scattered spectrum, the detailed analysis begins with the derivation of a cross section corresponding to each peak. Although nuclear levels are generally extremely well defined in energy, the peaks in these experiments always have a certain energy-breadth. This line-width depends on the exact experimental conditions—the energy width of the incident beam delivered by the focusing system; statistical variations of the energy lost to ionization and radiation by the electrons on traversing the target; and the resolution function of the spectrometer. In the absence of these effects, each peak would appear as a very narrow line in the spectrum, the width of each line being proportional to the probability of exciting the corresponding nuclear level. Since this probability is the object of the experiment in the first instance, it scarcely matters that the intrinsically sharp spectral line is blurred by these instrumental effects, provided that a correct evaluation of the total area under the peak can be made. Ambiguity need not arise as long as the instrumental line-width is less than the separation of adjacent spectral lines. The area under each peak, corrected for instrumental errors, is conveniently expressed in units of nuclear scattering cross section, roughly speaking the area in square centimetres presented by the nucleus to each electron in the incident beam. At the root of theoretical expressions for the cross section for scattering of charged particles is the famous formula of Rutherford,

$$\sigma_R(\theta) = \frac{z^2 Z^2 e^4}{16E^2} \frac{1}{\sin^4 \frac{1}{2}\theta} \qquad \ldots(1)$$

in which σ(θ) is the cross section for scattering incident point charged particles (charge ze) of kinetic energy E, against immovable charged point centres (charge Ze), through a polar angle θ. This is not, however, a relativistic formula and does not allow for the intrinsic degree of freedom possessed by an electron, namely its spin. These features are taken into account, with adequate approximation, in a similar expression derived by Mott,

$$\sigma_M(\theta) = \left(\frac{Ze^2}{2E}\right)^2 \frac{\cos^2 \frac{1}{2}\theta}{\sin^4 \frac{1}{2}\theta} \qquad \ldots(2)$$

However, when the nucleus can no longer be considered simply as a point charge, that is when anomalous scattering is observed, then, corresponding to equation 2, a scattering formula for a nucleus of finite size can be shown to be

$$\sigma_e(\theta) = \left(\frac{Ze^2}{2E}\right)^2 \frac{\cos^2 \frac{1}{2}\theta}{\sin^4 \frac{1}{2}\theta} \left[\int \rho(r) \exp(\hbar q.r) dr\right]^2 \qquad \ldots(3)$$

Here $\rho(r)$ is the charge density within a nucleus as a function of radius vector from the centre of the nucleus, and $\hbar q$ is the momentum transfer vector. The numerical magnitude of q for elastic scattering is given by

$$q = \frac{2E_i}{c} \sin \tfrac{1}{2}\theta \qquad \ldots(4)$$

and thus depends on the choice of E_i and θ. The integral in equation 3 reduces for spherically symmetric nuclei to the form

$$\sigma_e(\theta) = \left(\frac{Ze^2}{2E}\right)^2 \frac{\cos^2 \frac{1}{2}\theta}{\sin^4 \frac{1}{2}\theta} \left[\int_0^\infty \rho(r) \frac{\sin qr}{qr} 4\pi r^2 dr\right]^2 \qquad \ldots(5)$$

As the quantity in square brackets multiplies the point charge cross section of equation 2, it is customary to follow the precedent established in the electron diffraction and X-ray diffraction analogue of this equation and call the quantity,

$$F = \frac{4\pi}{q} \int \rho(r) \sin(qr) r dr \qquad \ldots(6)$$

the form factor or structure factor corresponding to the anomalous scattering for a finite nuclear charge distribution. This analogy is very close indeed, since one is merely replacing the electron cloud of an atom by the proton cloud of a nucleus.

The form factor is the meeting place of theory and experiment. The experimentalist measures the cross section and divides out the uninteresting part represented by $\sigma_M(\theta)$, due to the Coulomb deflection, and is left with the form factor. He measures F as a function of q, choosing E_i and θ to satisfy equation 4. The theorist begins with a nuclear model leading to the charge density $\rho(r)$ and then calculates F by evaluating the integral of equation 6. For light nuclei, this is a satisfactory procedure, while for medium and heavy nuclei, the expression for $\sigma_M(\theta)$ is no longer applicable owing to the greater distortion of the electron de Broglie waves by the more intense nuclear electromagnetic field. However, this distortion can be dealt with by a more precise treatment of the scattering problem which involves very

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high computational precision and is therefore performed with large computers. The end result is the same—a comparison of the form factor expected from a nuclear model with the experimental one, and adjustment of the model parameters until a best fit is obtained.

In a similar way, inelastic form factors are derived from inelastic scattering cross sections and are related to the changes in charge distribution occurring while the nucleus alters its internal state of motion from the ground state to the excited level. As two states of the nuclear motion are involved, inelastic form factors present quite different functional dependence on q from elastic form factors.

In addition to the scattering due to the Coulomb interaction between electron and nuclear charges, scattering due to interaction with nuclear magnetization distributions also occurs. Magnetic scattering in general has a different dependence on θ from charge scattering, a feature which is exploited to separate the two. Nuclear magnetization has two origins, either in the motion of the charged protons, or in the intrinsic magnetization of the neutrons and protons themselves. The study of magnetic scattering as a function of momentum transfer has made it possible in favourable cases to distinguish the two kinds of contribution, both for elastic and inelastic scattering.

One last feature of the scattered spectrum displayed in figure 3 occurs at values of E_f smaller than those corresponding to the inelastic peaks. The transition from a region characterized by the peaks to a region of slowly varying, featureless cross section is gradual, and occurs at different values of E_f from nucleus to nucleus. Whilst no outstanding feature occurs, the precise shape of this part of the scattering cross section is of great interest. It corresponds to energy transfers to the nucleus which are large enough to disrupt it completely and cause separation of the constituent nucleons. Generally speaking, this disintegration region begins at the threshold energy transfer corresponding to the binding energy of the nucleus, and extends up to transfer of almost the entire energy of the incident electron. This region is called the incoherent scattering continuum, and its relative contribution to the spectrum is determined by the value of momentum transfer in the experiment. The word 'incoherent' refers to the fact that the individual nucleons tend to scatter electrons independently of their neighbours; and the word 'continuum' is used to state that the system of nucleons can exist with any value of kinetic energy, rather than the discrete values of the weakly excited nucleus. Confirming this interpretation is the fact that the energy of the maximum of the continuum occurs almost at the energy E_f corresponding to elastic scattering on free protons in a hydrogen target. However, in a real nucleus, the nucleons are in motion initially relative to the incident electron direction owing to the internucleon forces. The effect of this internal motion is to broaden the continuum scattering into a distribution far wider than is observed from a hydrogen target. The exact shape depends on the initial momentum distribution of the neutrons and protons in the nucleus and permits measurement of this valuable information.

Results

In the course of some twelve years of exploitation of electron scattering, a great deal of diverse information concerning nuclear structure has been acquired. Among the results are the spatial distribution functions of nuclear charge and magnetization densities in the nuclear ground state; the charge and magnetization densities occurring when the nucleus changes from one state to another; and the state of internal motion of the constituent nucleons as manifested by their initial momentum distribution. These are all quantities or functions predicted by current nuclear theories and impose severe tests on them. Discussion of all of these results would take far too long, so we must limit ourselves to a consideration of the size and shape of nuclei in their ground states. The relevant experimental quantity is the elastic cross section, an example of which is given in figure 4. Referring to equation 3, it is easily seen that for a constant density $\rho(r)$, the form factor F exhibits a series of zeros as q increases. Zero values do not occur in experimental cross sections, since the densities $\rho(r)$ are not constant in the surface region and because of the corrections to equation 3 due to distortion of the electron waves. In their place remain pronounced minima at values of momentum transfer q which are easily related to the nuclear radius r.

Results for nuclear radii can be summed up in a systematic fashion, as, in general, all nuclei exhibit the same features. The radial charge distribution consists of two regions, an inner one of constant density, and an outer one where this density gradually tails off. Figure 5 illustrates the situation, which is summarized by specifying two parameters: c the value of nuclear radius at which the density is half of its central value, and t the thickness

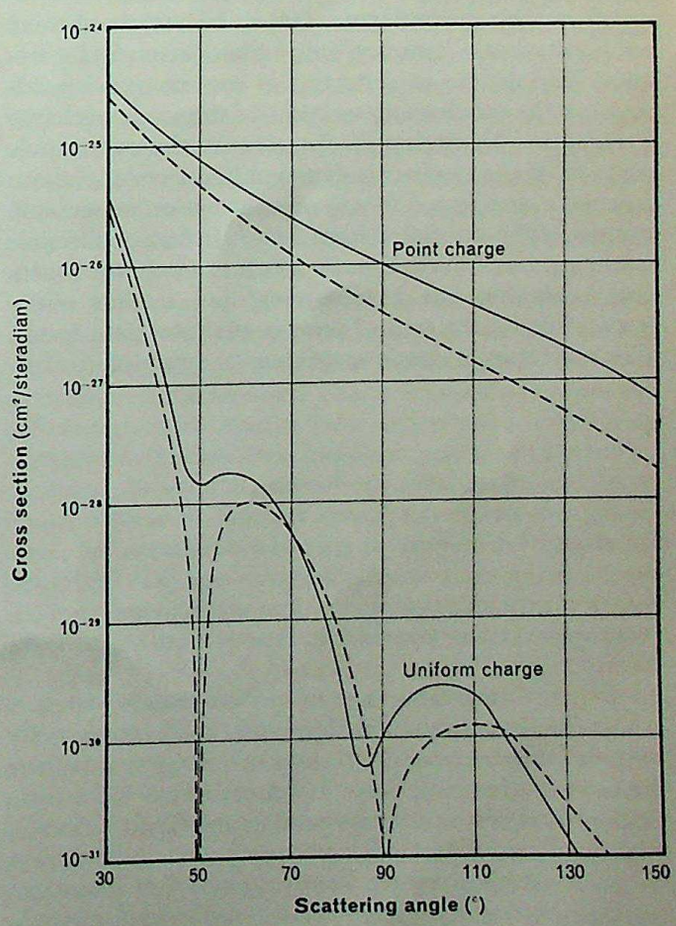

Figure 4 The change of cross section with scattering angle. The full line is the result of an exact calculation of the cross section for scattering 230 MeV electrons from copper. The dashed line is calculated from the formulae given in the text.

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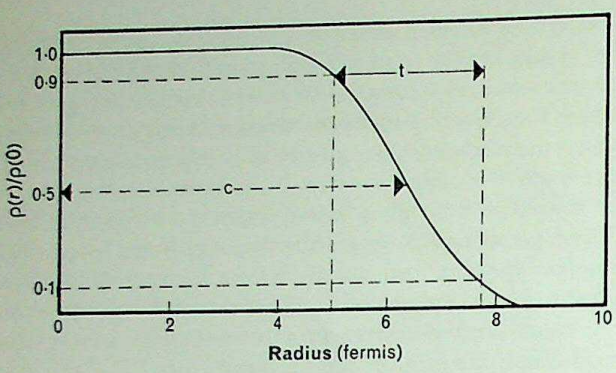

Figure 5 The density distribution of nuclear charge. Parameters c and t are shown. This figure is drawn for the gold nucleus, but all nuclei show these general features. ($\rho(0)$ is $\rho(r)$ when $r = 0$.)

of the outer region through which the density drops from 90 per cent to 10 per cent of its central value. The parameter c is found to be proportional on the average to $A^{1/3}$ (A is the atomic mass number), which is consistent with a constant density for nuclear matter. The parameter t is roughly constant for all nuclei and thus independent of A. Since A varies over two orders or magnitude for known nucleon species, this is a remarkable result. Variations from the average behaviour are, of course, found for small local regions of A. Thus the charge radii of isotopes such as O^{16}, O^{18}, and Ca^{40}, Ca^{42}, Ca^{44} do not vary strictly as $A^{1/3}$, but reflect structure features peculiar to these restricted ranges of A.

Not all nuclei necessarily have strict spherical symmetry in their ground state, and in fact many of them are permanently distorted into oblate or prolate ellipsoids. The degree of distortion is summarized by calculating the quadrupole moment of the nuclear charge distribution. Scattering of electrons by the quadrupole moment of the nucleus is distinguished from the above monopole case by a different dependence on momentum transfer of the associated form factor. In fact quadrupole scattering has a maximum for q-values where the monopole scattering has a minimum, and is thus partly responsible for the lack of zeros in the total form factor. The two forms of elastic scattering are straightforwardly separated, however, by their q-dependence, and the quadrupole moment of the nucleus measured directly, giving the exact deviations of the nucleus from spherical symmetry. Similar features are relevant to the magnetic scattering caused by the dipole and octupole moments of the nuclear magnetization density. In fact the octupole moments of light nuclei have never been measured by methods other than electron scattering.

Future work

Much of the initial work on electron scattering by nuclei has been performed during time borrowed from the programmes of elementary-particle study with the high-energy linear accelerators at Stanford and Orsay. For nuclear structure studies, the highest energies are not necessary, as an energy of 100–200 MeV with a highly refined beam is sufficient. Thus, in designing the second generation laboratories for nuclear studies, emphasis is placed on obtaining very high currents, two orders of magnitude greater than those of existing machines, so that extremely well resolved beams of adequate intensity are made available. At the same time, the high electron-current machine can be adapted to the production of usable beams of positrons which, since they are repelled by the positively-charged nucleus rather than attracted as are electrons, are likely to be useful probes of the more tenuous outer region of the nucleus. With new accelerators of high intensity coming shortly into operation at the Universities of Glasgow, Saskatchewan, and Toronto, and at the National Bureau of Standards in Washington, we can expect a flood of accurate and detailed information on how nuclei are put together from neutrons and protons.

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The cytoplasmic control of gene activity

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J. B. Gurdon

Although we now have much information on how instructions from genes are translated in a cell, very little is known of the mechanism that controls the activity of the genes. This article describes nuclear transplantation experiments which show that frog egg cytoplasm can exert this control, and that genes do not disappear from a specialized cell, but merely become inactive.

The characteristics of all living organisms, as well as of their component cells, are ultimately determined by genes. Although this statement has not been actually proved for all cell structures and all properties, it is certainly true in many cases, and no example is known in which it is false. A knowledge of the way genes work is therefore of fundamental importance in biology and medicine. There are two main aims in the study of gene action. One is to identify the steps by which a gene transmits information leading to the synthesis of a particular protein; the other is to determine what factors provide quantitative regulation of gene activity, that is, how much of each gene product is synthesized at different times in different cells. A lot of information about the translation of genetic information has accumulated in the last few years [15, 16], but very little is known about the way gene activity is regulated, especially in higher organisms.

The control of gene activity is best studied under conditions in which the activity of genes changes, as happens in the polytene chromosomes of certain insects [1], and during the formation of eggs in Amphibia [4], as well as following hormone administration in plants and animals [14]. One of the biological conditions in which the greatest changes in gene activity take place is during the early development of embryos, a time when very many different kinds of cells are being formed from a single fertilized egg. Embryologists have for a long time been aware that regional differences in egg cytoplasm must be at least partly responsible for making a population of apparently identical nuclei behave differently. In early development, the kind of cytoplasm in which a nucleus lies seems to determine which of its genes will be active.

The analysis of this interaction between the nucleus and cytoplasm of a cell would be much facilitated if we could exchange the nucleus of one cell for that of another. This is technically difficult to do, but owing to certain particularly favourable aspects of the design of their eggs, it can be achieved by nuclear transplantation in Amphibia.

The technique of nuclear transplantation in Amphibia

The first real success at transplanting living cell nuclei in Amphibia was achieved by R. Briggs and T. J. King [2], using the American frog *Rana pipiens*. The principle of their method has been employed with modifications in all subsequent work of this kind, including that done with the South African water frog. *Xenopus laevis*. The method consists of three stages, as illustrated in figure 1.

In order to prepare donor cells, a piece of tissue such as the endoderm of a tadpole is dissected out with fine needles, and the ectoderm and mesoderm cell layers are peeled away from it. It is then placed in a saline solution lacking calcium ions but containing versene. After about twenty minutes, the endoderm cells will separate from each other, because the versene removes the calcium ions that are necessary for cells to stick together as a tissue. The dissociated cells are transferred to a standard saline solution, where they can be kept for an hour or two until required for nuclear transplantation.

Unfertilized recipient eggs can be obtained by squeezing them out of *Rana* frogs, or by using hormone to induce *Xenopus* frogs to lay. The eggs have now to be enucleated; this can be done by removing the egg nucleus manually with a needle in *Rana* species, or by inactivating it with ultraviolet irradiation in *Xenopus* and other Amphibian genera. By using different genetic strains or subspecies for the recipient eggs and donor nuclei (see figure 1), it has been shown in *Xenopus* that the egg nucleus disappears soon after irradiation and does not participate in development [5, 8]. It has sometimes been suggested that the different methods of enucleation employed in *Rana* and *Xenopus* might account for the fact that enucleated eggs receiving transplanted nuclei develop more normally in *Xenopus* than they do in *Rana*. There are several reasons why this explanation is very unlikely to be correct, but one of the most convincing is the fact that eggs of the Axolotl, enucleated by ultraviolet irradiation, develop about as well after nuclear transplantation as do manually enucleated *Rana* eggs, but much less normally than do ultraviolet-enucleated *Xenopus* eggs.

The final stage in the method involves sucking a dissociated cell into a micropipette in such a way that the cell wall is broken, but the cell cytoplasm is not removed from around the nucleus. This is necessary because the cell nuclei of all multicellular organisms are seriously damaged if exposed even briefly to any kind of artificial medium. As a result, donor cell cytoplasm, as well as donor nucleus, is injected into the recipient egg. However, the amount is very small—about one fifty-thousandth of the egg cytoplasm—and it is known from the injection of donor cell cytoplasm alone that it has no effect on the development of nuclear-transplant embryos.

Induction of gene activity by egg cytoplasm

When nuclei from embryonic or tadpole cells are transplanted to eggs in this way, the resulting nuclear-transplant embryos sometimes develop normally, but sometimes do not. Those nuclear-transplant embryos that do develop in a normal way permit a very simple and clear conclusion to be drawn—that the transplanted nucleus, whatever kind of cell it has come from, has been made to behave as if it were the nucleus normally present in a fertilized egg. Normal nuclear-transplant embryo development has been obtained in several different kinds of Amphibia [11], but in most cases this is true only if nuclei

J. B. Gurdon, *M.A., D.Phil.*
Was born in 1933 and educated at Eton and Christ Church, Oxford. Apart from the tenure of a visiting research Fellowship at the California Institute of Technology from 1961 to 1962 and at the Carnegie Institution of Washington in Baltimore in 1965, he has carried out his research at Oxford University, where he is now a University Lecturer in the Department of Zoology, and a Research Fellow of Christ Church

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are taken from unspecialized embryonic cells, and not from adult tissues. In one case, however, it has been possible to obtain normal nuclear-transplant embryos from nuclei of a fully specialized cell—the intestinal epithelium cell of feeding *Xenopus* tadpoles. The nuclei of this kind of cell (figure 2) have produced the specialized structure of these cells, seen most clearly by the presence of the striated border found only in cells specialized for absorption. The genes that code for haemoglobin in blood cells, and for actin or myosin in muscle cells, either have become inactive in, or have disappeared from, the intestine cells. In spite of this, some of the enucleated eggs that receive transplanted intestine nuclei develop into entirely normal tadpoles, possessing both blood and muscle cells [9]. Some of these tadpoles have been grown up into fertile male and female frogs [13]; yet all the nuclei in these frogs are derived by mitosis from a single nucleus that was once part of an intestine cell. These experiments permit the following two conclusions to be drawn. Firstly, genes that are no longer required in development, for example haemoglobin genes in intestine cells, are not lost, but are conserved. Secondly, genes which would normally remain inactive in a specialized cell can nevertheless be made to become active by transplanting the nuclei in which they are contained to egg cytoplasm; examples of such genes are those that are present in intestine cells but are required only for the differentiation of muscle, blood, egg, and sperm cells.

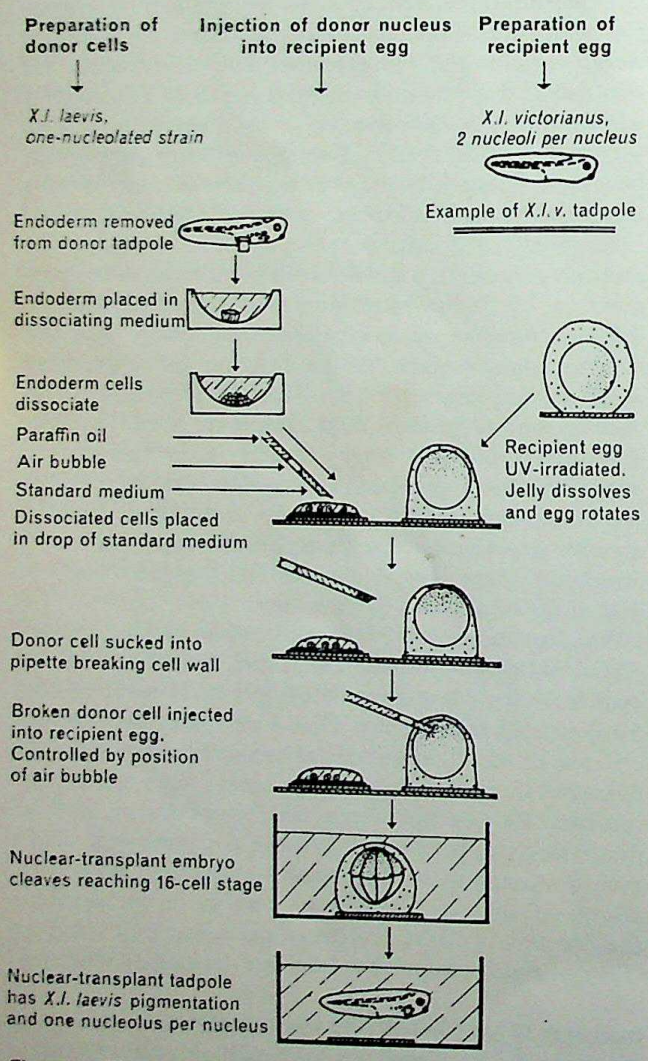

Figure 1 The principal stages involved in transplanting nuclei in *Xenopus laevis*. In this diagram donor nuclei are taken from a strain of the subspecies *Xenopus laevis laevis* which has only one nucleolus in each nucleus. The young tadpoles of this subspecies have many pigment cells on their body. Recipient eggs are taken from the subspecies *Xenopus laevis victorianus* in which nuclei of most diploid cells have two nucleoli, and in which the young tadpoles have no body pigment. The nuclear-transplant tadpoles have the characteristics of the nuclear, not the cytoplasmic, parent, showing that their nuclei are derived from the transplanted nucleus.

The proportion of transplanted nuclei that support normal nuclear-transplant embryo development is rarely more than 35 per cent, and is often only 1–2 per cent. This does not affect the validity of the conclusions drawn above, since the use of nuclei and eggs from different genetic strains of *Xenopus laevis* shows conclusively that the nuclei in a nuclear-transplant embryo are derived from an intestine cell nucleus and not from the egg nucleus. Actually it has been shown by serial nuclear transplantation and by a cytological analysis of eggs receiving transplanted nuclei that at least 70 per cent of *Xenopus* intestinal nuclei can support the development of nuclear-transplant embryos having normal muscle and nerve cells [9].

Repression of gene activity by egg cytoplasm

The experiments described above show that genes can be activated by egg cytoplasm, but this does not necessarily show that genes can also be 'turned off' by the same treatment. In collaboration with D. D. Brown, the following experiment was designed to investigate this [12]. Ribosomal RNA is almost certainly a direct product of nuclear genes. It happens that ribosomal RNA genes are active in embryos beyond the gastrula stage, and especially in tadpoles, but are totally inactive during cleavage. We therefore transplanted nuclei from tadpole cells into enucleated eggs and looked to see whether ribosomal RNA was synthesized during the cleavage of the resulting nuclear-transplant embryos. If the ribosomal RNA genes which are active in tadpoles are 'turned off' by the egg cytoplasm, then no ribosomal RNA would be synthesized by the nuclear-transplant embryos during cleavage. On the other hand, if genes which are once active always remain active, then ribosomal RNA would be synthesized actively during the cleavage of the nuclear-transplant embryos.

In order to do this experiment it is necessary to be able to determine whether an embryo is synthesizing ribosomal RNA or not. This is done by giving an embryo a radioactive substance that is a precursor of nucleic acid. This will be incorporated into all nucleic acids that it synthesizes after this time. In order to distinguish ribosomal RNA from other substances, a mixed population of all RNA molecules in an embryo is centrifuged through a thick solution of sucrose. Each kind of RNA molecule moves towards the bottom of the centrifuge tube at a speed largely determined by its size. Two main sizes of ribosomal RNA are present in animal cells, and these are seen in figure 3a as two peaks, the size of which indicates the amount of each kind of ribosomal RNA present.

When a swimming *Xenopus* tadpole is incubated in radioactive $Na_2{}^{14}CO_3$ for six hours, its endoderm cells synthesize a lot of ribosomal RNA, seen in figure 3a as two peaks of radioactive RNA. Nuclei from the endoderm cells of another tadpole of the same age were transplanted to enucleated eggs which contained radioactive

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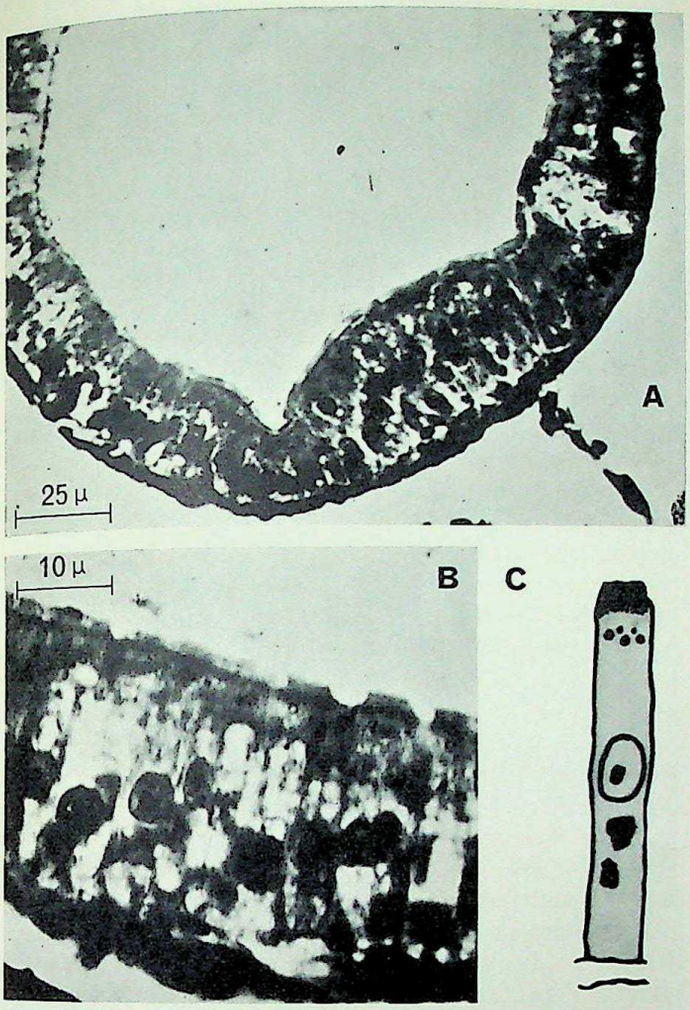

Figure 2 Intestinal epithelium of feeding tadpoles of *Xenopus laevis*. Transverse section of intestine—low power, A; high power, B. Figure C: diagram of single epithelium cell, like one seen in the centre of figure B, showing (from top to bottom) the striated border, pigment granules, nucleus, and yolk granules.

$^{32}PO_4$—a nucleic acid precursor. The resulting nuclear-transplant embryos synthesized no ribosomal RNA during the next six hours of cleavage (figure 3b). The egg cytoplasm had therefore 'turned off' the ribosomal RNA genes which were active in the tadpole endoderm cells. In another experiment, embryos obtained from the transplantation of tadpole nuclei were allowed to grow for two days into neurulae. These embryos were then found to contain radioactive ribosomal RNA (figure 3d), just as do neurulae reared directly from fertilized eggs (figure 3e). These experiments demonstrate a very precise control of gene activity by egg cytoplasm, since not only were previously active genes 'turned off' or repressed, but the same genes were made active again at a later stage in development when the cytoplasm of the embryo had changed.

Cytoplasmic induction of gene activity in cells of adult frogs

The conclusions reached so far all apply to cells which were taken from growing embryos or tadpoles, and which divide at least from time to time. In contrast the cells of adult frogs either never divide at all, for example red blood cells, or else they divide only very rarely, like those in the brain. In cells which have ceased division, genes no longer synthesize DNA, that is, they no longer make copies of themselves. We know of only two kinds of direct gene product—DNA and RNA, and it seems that the genes in many adult cells have lost the capacity to make the first of these. We would like to know if egg cytoplasm can activate genes responsible for DNA synthesis, as well as control their synthesis of RNA in the way described above. In order to answer this question we recently carried out the following experiments [7].

We have made use of the fact discovered by C. F. Graham [6] that, in fertilized eggs, there is a period of intense DNA synthesis by egg and sperm nuclei between 20 and 40 minutes after fertilization. When we injected nuclei from brain and blood cells of adult frogs into enucleated eggs, the great majority of these nuclei started to synthesize DNA within an hour. This was shown in the following way. Immediately after the injection of nuclei, some ^{3}H-thymidine, a specific DNA precursor molecule, was injected in to the same enucleated eggs. After an hour the injected eggs were fixed, sectioned, and autoradiographic film was placed over the sections. A

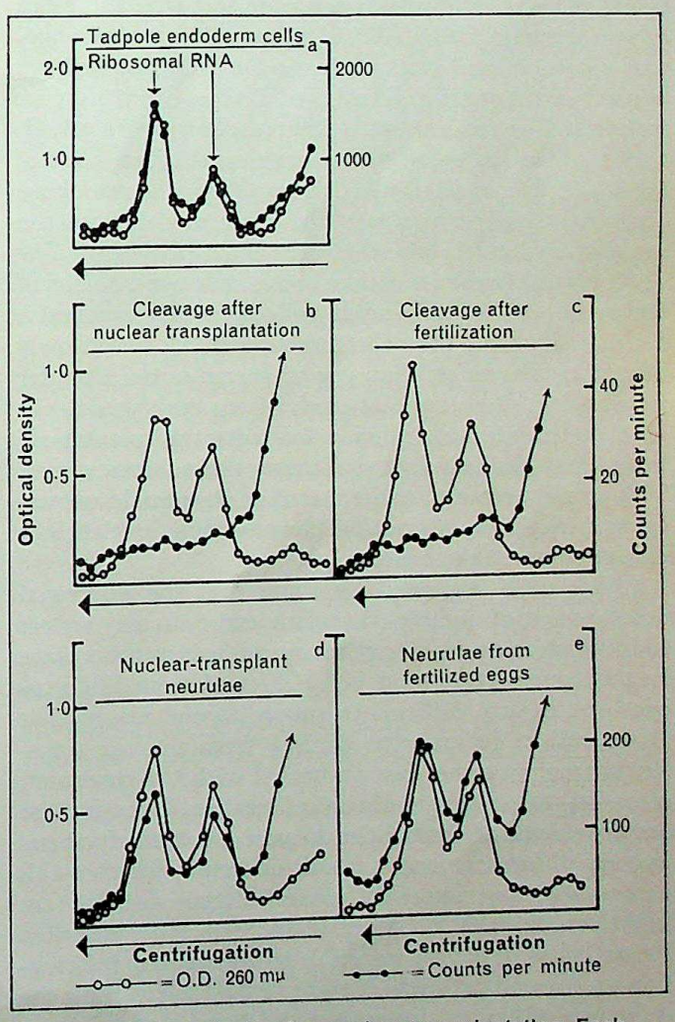

Figure 3 RNA synthesis after nuclear transplantation. Each figure shows the distribution of RNA molecules after centrifugation through a thick sucrose solution. o—o—o = optical density at 260 mμ. The two major peaks show the amount of the two main kinds of ribosomal RNA. The distribution of radioactive RNA molecules is shown in counts per minute by the solid dots (●—●—●). Figure 3a: RNA extracted from the endoderm cells of swimming tadpoles which had been incubated in radioactive medium for 6 hours. Figures 3b–3e: Eggs which received transplanted nuclei or which were fertilized contained a large store of radioactive RNA-precursor molecules ($^{32}PO_4$). RNA was extracted when these embryos reached the blastula stage (3b, 3c) or the young tadpole stage (3d, 3e). These figures are adapted from Gurdon and Brown [12].

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few weeks later the film was developed, and we could see large numbers of silver grains over the injected nuclei, showing that they had synthesized DNA (figure 4A–D). We were able to show that the observed DNA synthesis was not induced by the procedures used to prepare or inject the nuclei.

This result demonstrates a very powerful influence of egg cytoplasm over nuclear function, since less than 1 per cent of frog brain nuclei, and no red blood cell nuclei, normally synthesize DNA in any one hour period, and most of them would never do so in the rest of their life. Yet one hour after injection into frogs' eggs, over 70 per cent of these nuclei are induced to commence DNA synthesis.

Resistance of genes to complete control by egg cytoplasm

By no means all nuclei injected into *Xenopus laevis* eggs come immediately under the control of the egg cytoplasm. This is clearly shown by the fact that there are always some transplanted nuclei that fail to promote normal cleavage, and many others which do not support normal development of embryos derived from nuclear transfers. The same point is illustrated in figure 5A, B, which show that some nuclei have synthesized a lot of DNA 90 minutes after injection into eggs (the nuclei are obscured by silver grains); yet other nuclei from the same brain have synthesized very little (they show few silver grains) in the same time in the same eggs. Nuclei of embryonic as well as adult cells generally synthesize DNA, or replicate their chromosomes, much more slowly after transplantation than egg or sperm nuclei do after fertilization. It seems that nuclei from embryonic cells are sometimes forced to divide, following transplantation, before they have finished replicating their chromosomes. This would account for the fact that abnormal nuclear-transplant embryos usually have broken or deficient chromosomes in their nuclei [3].

It has been suggested by some that the abnormal development of nuclear-transplant embryos may reflect stable nuclear changes or gene repression that takes place in the course of normal cell differentiation. Unfortunately it is very difficult to prove beyond doubt that abnormalities in embryos derived from nuclear transfers are not in some way connected with the treatment of nuclei in the course of transplantation. Even if these developmental abnormalities do arise as a kind of natural nuclear differentiation, it is still uncertain whether this tells us anything about the control of gene activity that is concerned with bringing about cell differentiation. Nevertheless, it is very desirable to accumulate information on the extent to which transplanted nuclei resist the influence of egg cytoplasm, in the hope that this may prove relevant to the normal control of gene activity.

Prospects

The effect of *Xenopus* egg cytoplasm on nuclei injected into it appears to provide a particularly favourable opportunity for identifying the component of egg cytoplasm that controls gene activity. It is of great importance to remember that this effect of egg cytoplasm constitutes a completely normal response (DNA synthesis by living transplanted nuclei) to normal cytoplasm.

Although we know nothing so far of the cytoplasmic component which induces DNA synthesis, we can already

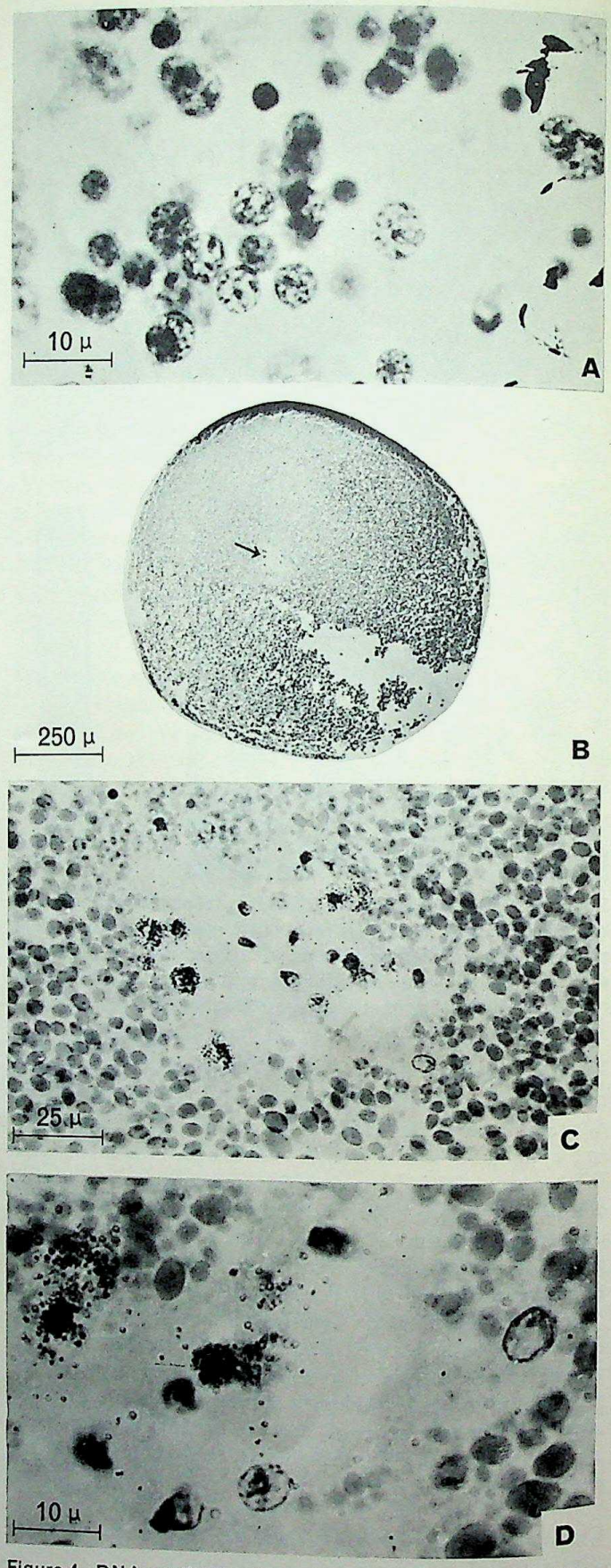

Figure 4 DNA synthesis after nuclear transplantation. Nuclei from glial and neuron cells (A) of *Xenopus laevis* are isolated and injected into unfertilized enucleated *Xenopus* eggs at the same time as some ^{3}H-thymidine. After 90 minutes the eggs are fixed, sectioned, and covered with autoradiographic film. Nuclei can be recognized by the mass of autoradiographic grains over them; they are very small in relation to the egg (B, arrow), and are well mixed with the egg cytoplasm (C, D).

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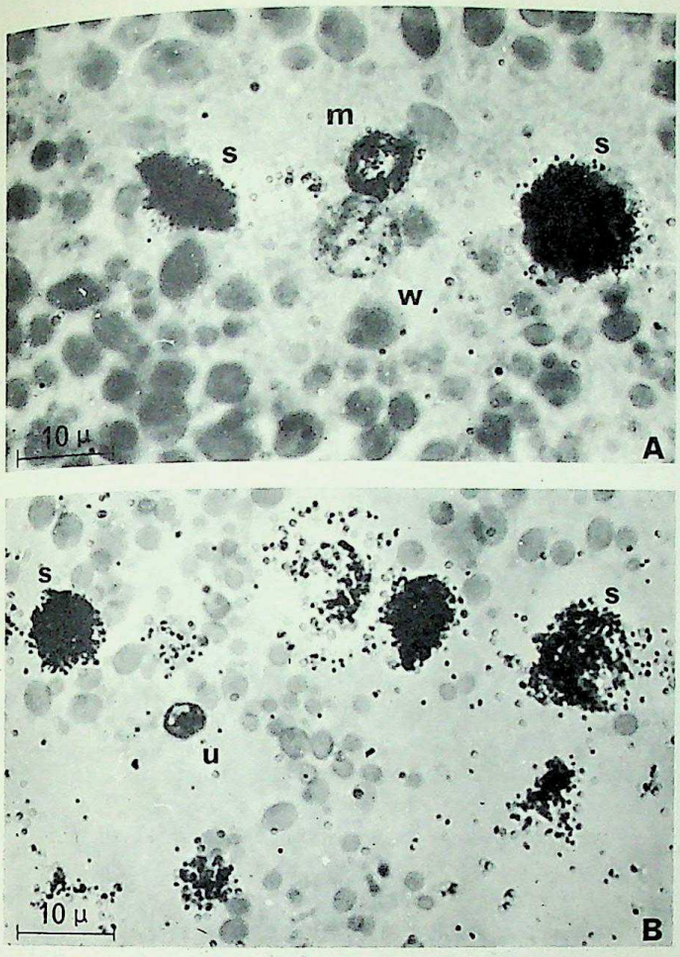

Figure 5 Autoradiographs of *Xenopus laevis* brain nuclei 90 minutes after injection into two enucleated unfertilized eggs. ^{3}H-thymidine was injected just after the brain nuclei. A great variation is seen in the amount of ^{3}H-thymidine incorporation by nuclei in the same egg. The nuclei shown are unlabelled (u), weakly labelled (w), medium labelled (m), or strongly labelled (s).

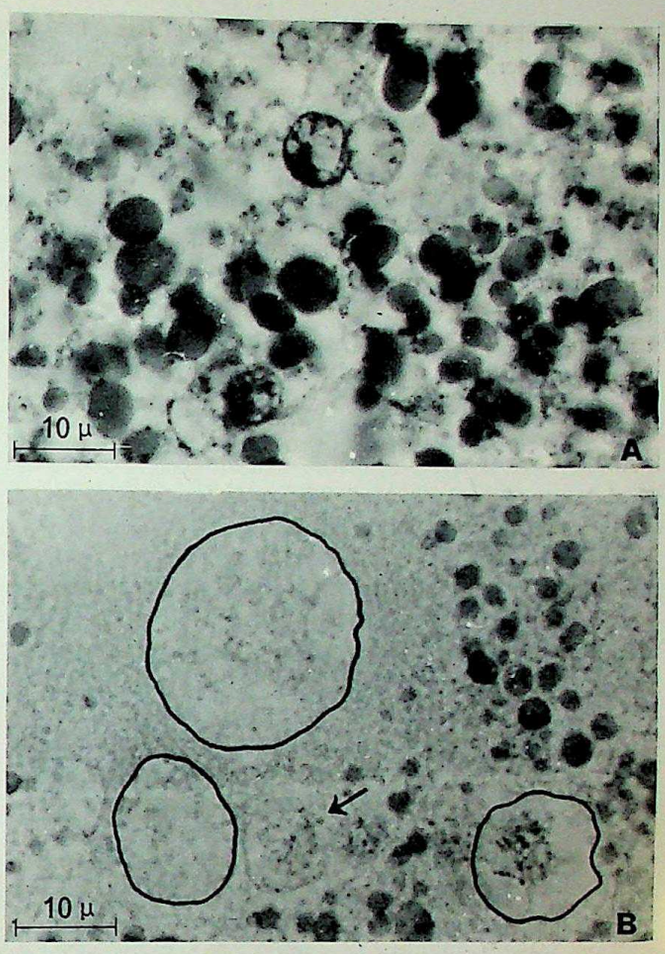

Figure 6 Swelling of brain nuclei after injection into unfertilized enucleated eggs. A shows brain nuclei 30 minutes after injection. These have swollen very little. B shows brain nuclei 90 minutes after injection. These have swollen to various degrees, as a result of which the nuclear membrane stains less strongly, and has been outlined in black. The arrow shows a slightly swollen nucleus which has not been outlined in black.

make one generalization about the process involved. It was observed some time ago [10] that nuclei transplanted to *Xenopus* egg cytoplasm undergo a rapid and pronounced increase in volume. The same observation has been made in blood, brain, and liver nuclei, which, after injection into eggs, sometimes swell to as much as 60 times their original volume in 90 minutes (figure 6A, B). We find that the degree of swelling of an injected nucleus is always related to the rate at which it synthesizes DNA [7]. The significance of this nuclear swelling can probably be explained in one of the following two ways. The swelling may be associated with an increased hydration, or some other change, in the nucleo-protein, which could alter the priming properties of the DNA. Another, perhaps more likely, suggestion is that the nuclear swelling necessarily involves the entry into the transplanted nucleus of some cytoplasmic components which may be responsible for the change in gene activity.

A good understanding of the way cytoplasmic components can control gene activity is of great importance not only because much of embryonic development and cell differentiation depends upon processes of this kind, but also because few other conditions are known in which the activity of genes can be altered in a predictable way.

Acknowledgment

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The early years of the *Académie des Sciences*

Douglas McKie

The *Académie des Sciences* was founded three hundred years ago, and it is thus one of the two oldest scientific societies in the world. Unlike its contemporary, the Royal Society, the *Académie* had a long list of duties and regulations, and was lavishly endowed by King Louis XIV. This article describes the early years of the *Académie*, and also the publication of the first scientific periodical.

This year, the world of science celebrates the tercentenary of the foundation of the national scientific academy of France, the *Académie des Sciences*. Founded in Paris in 1666 by the '*Roi Soleil*', King Louis XIV, on the advice of Colbert, his famous Minister, the *Académie* was established only a few years after the Royal Society of London, which was founded in 1660 and received its first Charter from King Charles II in 1662. The *Académie* and the Royal Society have had many active contacts with one another from their earliest years and, after three centuries of high distinction, remain not only the oldest but also among the most important scientific societies in the world.

While the origins of both societies, and of some similar but unsuccessful foundations, reflected the increasingly lively interest in 'natural philosophy' that first arose in sixteenth century Italy and afterwards passed to France and England, the conditions in all three countries differed greatly. The earliest scientific society, a small group calling themselves the *Academia Secretorum Naturae*, was founded in Naples in 1560 by Giambattista della Porta (1538–1615); its restriction of membership to those who had some discovery or observation to report gives a glimpse of what was to come afterwards. Unfortunately, the Church was suspicious and the academy was forced to end its meetings. Later Italian scientific societies met with greater, but still not lasting, success. The *Accademia dei Lincei* or Academy of the Lynx, so called from its emblem, founded in Rome about 1600 or 1603, continued with varying fortunes through many difficulties until 1657; it has since been refounded. The more famous *Accademia del Cimento* or Academy of Experiment, founded in Florence in 1657, came to an end in 1667 after ten successful years, terminated like Porta's Academy, it is alleged, by clerical opposition. However, both the *Lincei* and the *Cimento* had published their work or some part of it in volumes now regarded as among the classics of science, and this activity foreshadowed the future.

Where Naples, Rome, and Florence had in turn failed to achieve the secure establishment of a scientific society, London and Paris succeeded, but in very different conditions. In England, there was only one group assembling for scientific experiments and discussions. The members began to meet in Gresham College, London, in the 1640s. After many vicissitudes during the Civil Wars, when some members migrated to Oxford, they reassembled in Gresham College in 1660 after the Restoration of Charles II, and there the Royal Society was founded. In France, the situation was different. In the earlier half of the seventeenth century there was not one group of natural philosophers assembling for meetings, but many. While much of this interest was of an amateur and dilettante nature, it was certainly not everywhere so, and the groups were notably important in Paris. Scientific friends met there in association with de Thou and with the brothers Pierre and Jacques Dupuy; Descartes held meetings in his lodgings about 1626; Renaudot organized others in the *Bureau d'Adresse*; Marin Mersenne, the tireless scientific correspondent and Minorite father, held meetings in his cell; other assemblies were held in the house of Montmor; Henri Justel held similar meetings; and the Abbé Bourdelot set up an academy.

Such scientific activity led Colbert to advise the King to establish an official academy for the sciences and, it is to be noted, for their application to industry in order to increase the manufactures and exports of France. The utilitarian motive was as clear here, if not clearer, as it was in the establishment of the Royal Society. And so the *Académie Royale des Sciences* was founded in Paris in 1666, the minutes of the first meeting being dated 22 December of that year.

The membership was small and consisted almost entirely of scientists, unlike the Royal Society, where interest in science rather than attainments could procure admission to the Fellowship. The first members of the *Académie* numbered a mere twenty-one, including astronomers, mathematicians, chemists, anatomists, two physicians, one physicist, one botanist, and the great Dutch scientist Christiaan Huygens, specially invited to join the company. Others were elected later. The method of election is not known, but the *Académie* appears to have had a free hand in this matter. Members received pensions or salaries from the King, and the expenses of their experiments were provided for. In contrast, the Royal Society at this time was very short of money, as there were so many claims on Charles II's resources.

The *Académie* soon set to work in earnest. Colbert gave suitable accommodation in the *Bibliothèque du Roi* in the rue Vivienne, near the present site of the *Bibliothèque Nationale*. Meetings were held twice a week for experiments and observations. Soon after this the Observatory was erected south of the river, the foundations being laid in 1667 and the building completed in 1672.

The first publications of work done by the *Académie* included some remarkable volumes, large and sumptuously bound elephant folios, printed at the King's expense and mostly presented to those who were interested in such matters. For their illustration, the engraver appointed was Sébastien le Clerc, again at the King's expense. Louis XIV's patronage of his new *Académie Royale des Sciences* was lavish, very different from the state of affairs in London. Among these volumes we may mention two, the *Mémoires pour servir à l'histoire naturelle des*

Douglas McKie, *Ph.D., D.Sc., F.R.I.C., F.S.A., F.R.S.E.*
Was born in 1896. He entered University College, London, in 1920, graduated in chemistry, and was Professor of the History and Philosophy of Science in the University of London from 1957 to 1964. He is now an Emeritus Professor. He has written extensively on the history of chemistry.

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Figure 1 Louis XIV visits the *Académie Royale des Sciences* on 5 December 1681. (Reproduced from an engraving by Sébastien Le Clerc (1637–1714), by courtesy of the *Bibliothèque Nationale*, Paris.)

animaux (Paris, 1671), edited by Claude Perrault, and the *Mémoires pour servir à l'histoire des plantes* (Paris, 1676), edited by Dodart. These are almost certainly the two most magnificently published works in the whole literature of science. Each of them has a frontispiece, apparently of a later date, engraved by Le Clerc and recording the King's visit to the *Académie* in 1681 (figure 1). This is the only illustration we have of a meeting of a seventeenth-century scientific society. The figures are all drawn from life. The collection of instruments, apparatus, and specimens is most impressive, and the Observatory, although completed earlier, is depicted rising in the distance.

There are also two other engravings by Le Clerc showing the members of the *Académie* at work, again the only such illustrations we have of a scientific society at its labours in the seventeenth century, and, in fact, working in their dissecting-room and in their chemical laboratory. The first of these shows the anatomists dissecting an otter (figure 2); the other (figure 3) shows the chemists at work, and in this instance the apparatus and equipment of the chemical laboratory reveal the excellent conditions in which the members of the *Académie* pursued their researches, and the generous patronage under which they worked. The figures depicted in broad-brimmed hats in these two engravings are members of the Court, a further indication of the close relations between the King and his *Académie*. The *Académie*, as will be clear from these illustrations, flourished around an excellent dissecting-room and a well-equipped chemical laboratory, and it is recognized that the modern study of comparative anatomy began in this dissecting-room. The work of the *Académie* was very different from that of our contemporary scientific societies, and its life was much more like that of a national institute of research. Moreover, the experiments and observations were made in collaboration by all the members present, and nothing was set down in the *procès-verbaux* that was merely opinion and not fact, observed and verified in common.

However, another kind of publication was needed. These great books required time and labour to prepare and print. There were shorter and no less important scientific discoveries and observations that demanded more rapid publication and circulation. Even before the *Académie* was formally established in 1666, the interest of those who were actively concerned in these pursuits had led to the publication of the first scientific periodical, the *Journal des Sçavans*, ancestor of a tremendous progeny.

The *Journal* gave literary as well as scientific news and also information about new books, about experiments in physics and in chemistry, about discoveries in the arts and in the sciences, about machines and inventions, about the progress of mathematics, and about astronomical and anatomical observations. But it included also legal and ecclesiastical news and other matters, and was thus not entirely scientific, catering rather for the general interests of cultured readers. The founders gave much consideration to the question of whether the *Journal* should appear weekly, monthly, or annually; they decided on weekly publication, because such matter as they proposed to include might lose its interest or novelty in a month and still more so in a year, and they doubted whether an annual volume of this kind would attract the readers whom they had in mind.

This promising plan was not, however, as successful as had been expected. Although the first number was published on 5 January 1665, difficulties followed the thirteenth number, which appeared on 30 March 1665. The freedom that the editors had allowed themselves

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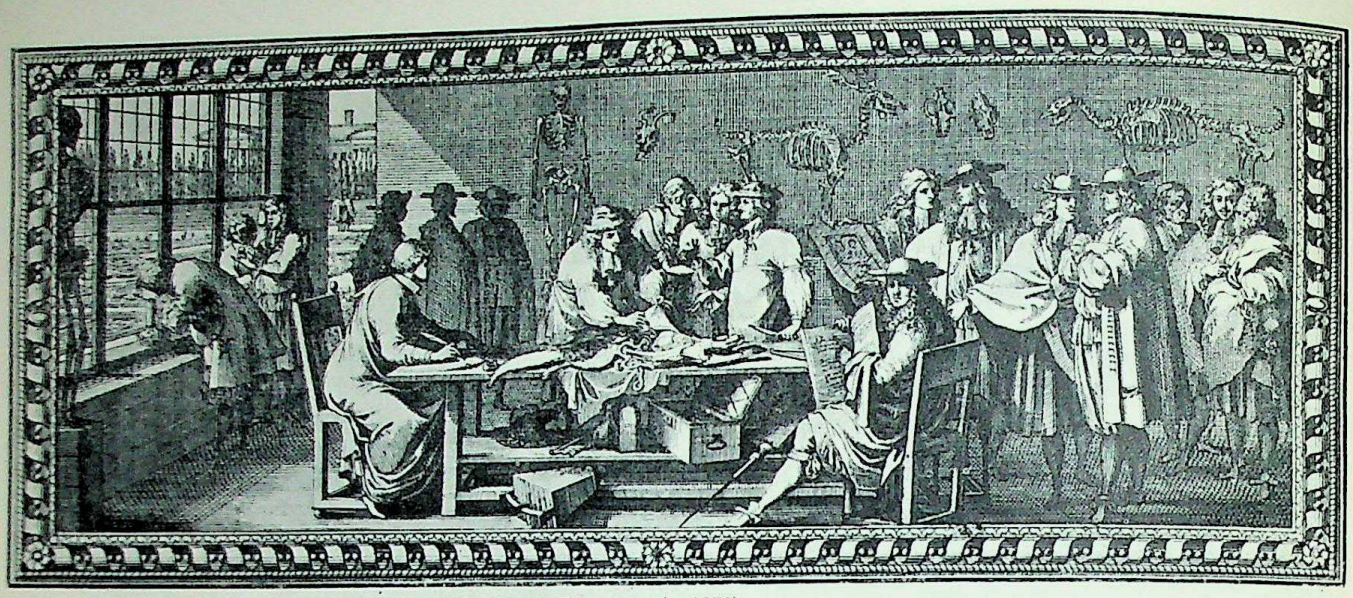

Figure 2 The anatomists of the *Académie* in their dissecting room (c. 1671).

Figure 3 The chemists of the *Académie* in their laboratory (c. 1676).

Figures 2 and 3 are reproduced from engravings by Le Clerc, by courtesy of the Trustees of the British Museum.

led to criticism and, it is said, to a clerical demand for censorship because of a disrespectful comment on the Inquisition. The *Journal* was suppressed for some reason or other, but it resumed publication on 4 January 1666 and continued to appear until it was again suppressed during the Revolution. It began to appear again in 1816, and later it became largely a literary periodical.

The most immediate and most important consequence of the first publication of the *Journal* on 5 January 1665 was to expedite a delayed decision by the Royal Society of London to publish a scientific periodical. Having seen a copy of the *Journal*, the Society decided to publish a monthly periodical strictly scientific in its content and appeal, and the first issue of the *Philosophical Transactions* thus appeared on 6 March 1665. It is interesting to note that, just as the *Journal* was the work of interested persons outside the *Académie*, so also the *Philosophical Transactions* was not an official publication of the Royal Society, but the private responsibility of the Society's Secretary, Henry Oldenburg. This historic publication continues to this day, the oldest of its kind.

As the seventeenth century drew to its close, there was a sense of dissatisfaction in Paris with regard to the publications of the *Académie*. These great volumes on animals, on plants, and on a number of other scientific investigations had added, it was recognized, to the glory of France and to the prestige of the *Académie*, but while such magnificent researches were a matter of high congratulation to all concerned, the understanding, appreciation, and knowledge of science were still confined to those who were engaged in pursuing such investigations. In other words, these volumes were read only by the members of the *Académie* and by similar specialists.

Accordingly the President of the *Académie*, the Abbé Bignon, after discussion with the Minister, the Comte de Pontchartrain, received the advice that someone should be appointed with the ability to explain in more suitable terms what seemed difficult and obscure in the publications of the *Académie*. A historic choice was made when Fontenelle was named for this task. The immediate result was that from 1699 annual volumes appeared in the famous series, *Histoire et Mémoires de l'Académie Royale des Sciences*. The second part of each volume contained the *Mémoires*, which were papers like those published in the *Philosophical Transactions*, and this part was separately paginated. The first part, the *Histoire*, gave, for the

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cultured reader not engaged in original scientific studies, a general historical account of the work done by the *Académie* in the different sciences during the year with which the volume was concerned, with cross-references to the *Mémoires* in the second part. This arrangement was successfully followed by Fontenelle and his successors until the *Académie* was suppressed during the Revolution. The *Histoire* was no trivial work of popularization, and sometimes it amounted to as much as a quarter of the complete annual volume.

At the same time, in 1699, the *Académie* was reorganized, or rather organized for the first time, and came more directly under the King's control as well as under his protection. There were to be in future four classes of members: ten honorary academicians, resident in France and distinguished in science, one of whom was to be President; twenty *pensionnaires* or salaried members, all resident in Paris; twenty *associés* or associates, twelve resident in France while the remaining eight might be foreign associates; and twenty *élèves* or pupils, all residing in Paris. Places in these last three groups were allotted to the different sciences to secure adequate representation of each science. The *pensionnaires* comprised three in each of the sciences of geometry, astronomy, mechanics, anatomy, chemistry, and botany, together with a permanent secretary and a permanent treasurer. The twelve French *associés* included two in each of the six sciences already named, while the eight foreign ones were not restricted to any particular science. Each of the twenty *élèves* (a term that was later to cause some heart searching) was to be closely associated with one of the *pensionnaires* in whose field of science he worked. Vacancies among *pensionnaires* and *associés* would be filled from the grade immediately below; those among the *élèves* would be filled on the recommendation of the *pensionnaires;* but in all instances the *Académie* merely proposed and the King decided. *Pensionnaires* and *associés* must have already gained some scientific reputation, and every member must choose some special problem of study and research. It now became the duty of the *Académie* to read the work published by scientists in other parts of France and in other countries and to report thereon. All experiments reported by members of the *Académie* must be verified in the presence of their fellow members; all observations made at meetings must be recorded in writing; differences of opinion must be dealt with courteously. The *Académie* must examine all works prepared for publication by its members and report on these at meetings; and, if a work was not approved, then the author was forbidden to describe himself on the title-page as a member of the *Académie* if it was subsequently published. All inventions for which a *privilège* of manufacture was sought must be examined by the *Académie* and reports must be made on their novelty and utility; without the approval of the *Académie* no *privilège* would be granted; and it was thus that the *Académie* began its long-enduring interest in inventions and in the mechanical arts, these duties constituting the *Académie* a kind of state office for the granting of patent-rights. The payment of salaries and of the expenses of experiments was continued. This lengthy *règlement* with its fifty clauses, including many details of days and times of meetings and of vacations, established the *Académie* in its definitive form, and later changes have not greatly altered its constitution in any really essential principle.

Organization on this scale, however, with very detailed regulations and with new and extensive duties prescribed, clearly necessitated larger accommodation, and the King therefore gave the *Académie* rooms in the *Louvre*. Here every member could pursue his own researches and here was housed the *Académie*'s great collection of instruments and apparatus, anatomical specimens, and machines. The royal munificence was thus continued and the *Académie* entered upon one of its most distinguished phases. The first meeting in the new quarters was held on 29 April 1699 and a medal was struck to commemorate this historic occasion. Effectively, a national centre of scientific research, fully equipped and provided with funds, had been established.

Some changes followed during the eighteenth century. In 1716 the title *élève* was abandoned as inappropriate and replaced by that of *adjoint* or assistant. There were also some slight changes in the representation of the different sciences. Also, although in 1699 the members were instructed to establish correspondence with scientists in France and abroad, the class of *correspondant* was not formally established until 1753. Such *correspondants* must be men of established scientific reputation living at a distance from Paris. Then in 1785 a considerable extension took place, in which, apart from annual and permanent office-holders, the ordinary academicians were grouped according to their sciences into eight classes, each consisting of three *pensionnaires* and three *associés*, making forty-eight such members; there were also twelve honorary members, seven senior *pensionnaires*, twelve *académiciens libres*, three senior *associés*, eight foreign *associés*, and one *associé* for geography.

This very satisfactory new constitution was, however, short-lived; for on 8 August 1793 the *Académie* with all other societies and academies of the old régime was suppressed by the Revolutionary government in spite of heroic efforts by Lavoisier to save it from extinction. Suppression did not last long, and the *Académie* was allowed to resume its functions in 1795 as one of the national academies in the newly created *Institut de France*. Eventually, with rooms in the former *Collège de Quatre-Nations*, it shared accommodation in this historic building, now generally known as the *Institut*, with the other national academies. In the new arrangement there were to be sixty members resident in Paris, eight foreign associates, and sixty non-resident associates, later renamed *correspondants*, living in France but outside Paris. Although the number of *correspondants* has since been raised to a hundred and twenty, the membership of the *Académie* itself remains about one hundred. Thus something of the traditional restriction of membership persists.

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Reversals of the earth's magnetic field

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R. L. Wilson and S. E. Haggerty

Studies in the magnetization of rocks raise some interesting problems. The rocks often show magnetizations that are reversed, compared to the ones that accord with the earth's present magnetic field. There are two theories—'field reversal' and 'self reversal'—that account for the finding, and this article discusses the evidence for, and the conflict between, these two theories.

Many rocks contain traces of iron oxides[1] that can be magnetized, and the natural magnetization of certain rocks—chiefly lavas and red sandstones—preserves for us the history of the magnetic field of the earth. Modern techniques are able to provide, for example, reliable information about the intensity of the field and about its variations during geological time. Even before the development of these rather difficult techniques, another curious phenomenon had been well known for several years—half of the rocks all over the earth's surface, of whatever age, are magnetized in the 'wrong' sense. Their directions of magnetization are antiparallel to the direction they would assume in the present 'normal' magnetic field (taking continental movements into account, of course). These rocks were termed 'reversed' rocks, and the others were termed 'normal' rocks—consistent, that is, with the present arbitrarily labelled 'normal' field polarity.

What was the significance of the existence of reversely magnetized rocks? Attempts to explain their occurrence by the literal overturning of blocks of magnetized lava failed because reversed rocks occur so frequently, and because their magnetization is too precisely reversed. There remained only two general possible explanations: either the reversed magnetization is a record of an inversion of polarity of the earth's magnetic field as a whole, or reversal of magnetization has occurred spontaneously in some rock magnetic minerals, due to some physical-chemical mechanism. Such 'self-reversal' mechanisms are known to exist in rare instances.

If both field reversal and self-reversal have occurred, then the situation is very complex, and requires a great deal of experimental unravelling. The actual evidence indicates an even more acute problem. There are sets of lavas (some normally and some reversely magnetized) from the same locality that give evidence to support both external field reversal and self-reversal within the specimens. The aim of this article is to survey the evidence for each of the mechanisms.

[1] The following minerals are referred to in this article:
Titanomagnetite: a member of the ulvöspinel (Fe_2TiO_4)-magnetite (Fe_3O_4) solid solution series.
Ilmenite ($FeTiO_3$): a solid solution series with haematite (Fe_2O_3).
Titanohaematite: a Ti-rich Fe_2O_3.
Pseudobrookite: lies between Fe_2TiO_5 and $FeTi_2O_5$.
Rutile: TiO_2.
Spinel: $(Mg,Fe)(Al,Cr)_2O_4$.
Maghaemite: γFe_2O_3.

R. L. Wilson, *Ph.D.*
Was born in St Thomas, Ontario, Canada, in 1929, and educated at the University of Western Ontario, McGill University, and Imperial College, London. He remained at Imperial College until 1963, when he moved to Liverpool to carry on studies in palaeomagnetism. His special concern is a reconstruction of the history of the earth's magnetic field – its polarity, intensity, and non-dipole irregularities – during geological time.

S. E. Haggerty, *B.Sc.*
Was born in 1938 in Germiston, South Africa, and entered Imperial College as an undergraduate in 1961. His Ph.D. research project is a study of the ferromagnetic minerals in basaltic lavas.

The evidence for field reversal

This evidence falls under six headings. Firstly, within the accuracy of present dating methods, rocks of similar age from any part of the world have the same polarity of magnetization. It is very unlikely that widely separated rocks have been subjected to the same causes of chemical change, and it is much more probable that changes in the external magnetic field have caused simultaneous reversals of polarity. For technical reasons only, the data at present available are limited to the past four million years and a long period of Permo-Carboniferous times. In addition, historic lavas or other materials known to have become magnetized in the present normal field have been found to have normal polarity.

A second piece of evidence is that underlying rocks that have always been baked by overlying lavas have consistently the same polarity as that of the baking rock. The heating would have destroyed any natural magnetization, so that both rocks, on cooling, would have been magnetized in the same sense. Half of the world's rocks are reversely magnetized, and if self-reversal were the mechanism, it would often produce baked and baking rocks of opposite polarities. However, there are more than 100 examples of agreeing polarity, a strong indication of field reversal.

Evidence that is closely related to the last is that certain rocks may contain two superimposed magnetizations which are due to a complex thermal history, and which were acquired at two separate moments in the history of

Figures 1–9 (All photomicrographs were taken using an oil-immersion objective. The scale line shows 25 μ.) Examples from basalt lavas of the progressive high-temperature oxidation of titanomagnetite (figure 1) to the highest oxidation state (pseudobrookite and titanohaematite intergrowths in figure 9). From figure 3 the oxidation may progress in various ways, for example figures 3, 4, 7, or 3, 5, 6. But all routes eventually lead to the highest oxidation state. Oxidation of this kind is not due to weathering of the basalt, but takes place at temperatures of 600–1000°C during the initial cooling of the lava.

1 A brown homogeneous titanomagnetite grain with sharp well-formed crystal faces. Titanomagnetite has a face-centred cubic structure.

2 Light-coloured crystallographically oriented lamellae of ilmenite along {111} planes in titanomagnetite. This is the first stage of high-temperature oxidation. Such a grain might have only one lamella, or might be packed solidly with them.

3 A well-shaped titanomagnetite grain with coarse ilmenite lamellae along {111} planes. The fine needles are short lamellae of spinel exsolved along the {100} cube faces.

4 The original broad ilmenite lamellae have been oxidized to pseudobrookite (grey) and a submicroscopic intergrowth ('metailmenite') of rutile and titanohaematite (yellow). Brown titanomagnetite again contains dark spinel rods.

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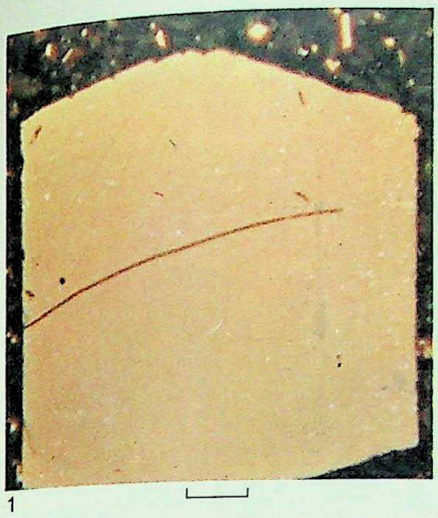
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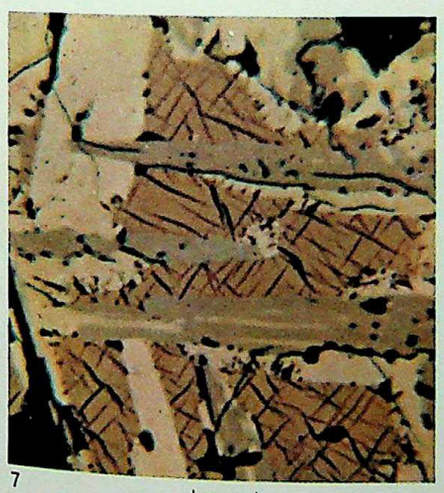
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5 Triangular brown titanomagnetite areas still contain spinel rods, but are being oxidized at their borders (see especially the point marked with the black arrow) to a yellowish submicroscopic intergrowth of titanohaematite (predominantly) and rutile. The original coarse ilmenite lamellae have passed beyond the 'metailmenite' stage of figure 4, and are now an easily visible streaky intergrowth of rutile (predominantly) and titanohaematite.

6 The smaller dark brown titanomagnetite areas have been enveloped by the streaky rutile-titanohaematite intergrowth. The larger titanomagnetite areas still survive.

7 Development of pseudobrookite (grey) and titanohaematite (bright yellowish) from the 'metailmenite' of figure 4. Titanomagnetite contains well-formed and abundant dark exsolved spinel rods.

8 A well-formed grain, originally titanomagnetite – the skeletal fern-like growth at the lower left corner is typical of titanomagnetite development. The grain is now in almost the highest oxidation state, containing pseudobrookite (grey) and titanohaematite (bright yellowish), but retaining two small brown patches and several long thin areas of titanomagnetite. The structure is controlled by the orientation of the original ilmenite lamellae along {111} planes.

9 This represents the highest oxidation state in the titanomagnetite series. The pseudobrookite (grey) has become redistributed into fewer, larger, more irregular areas in a host of titanohaematite.

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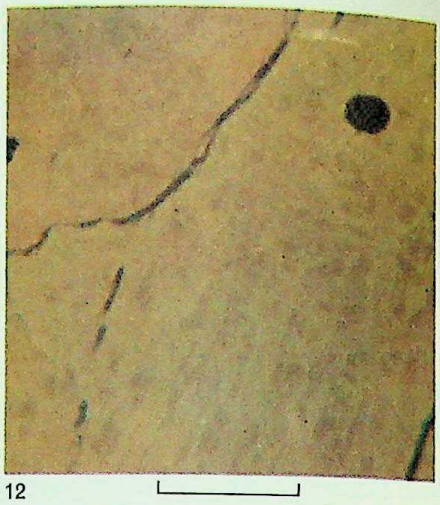
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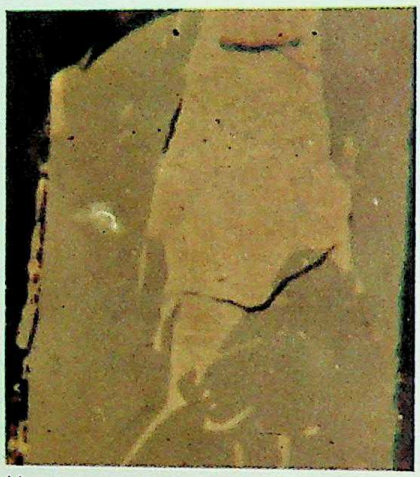
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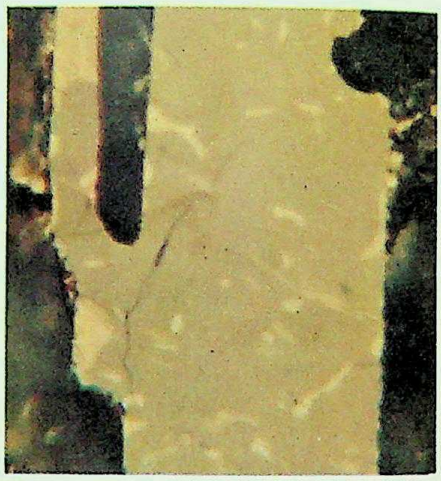
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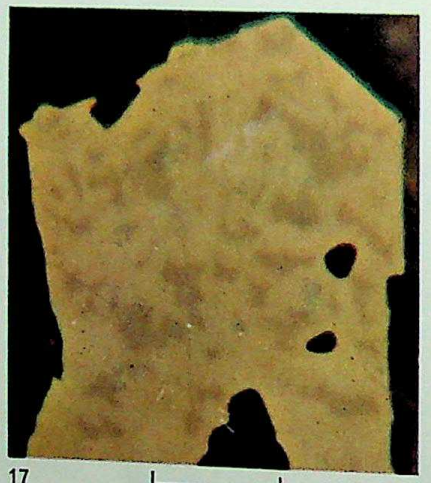
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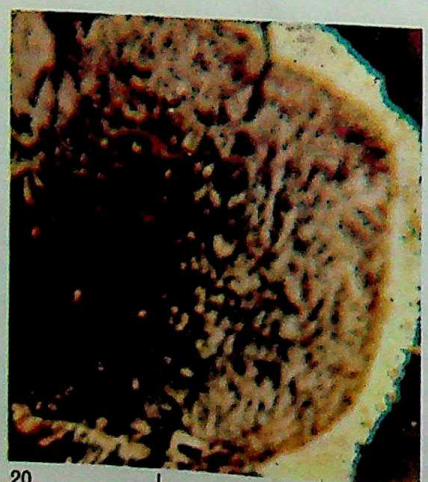
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Figures 10–15 Progressive high-temperature oxidation in discrete ilmenite grains.

10 Homogeneous skeletal ilmenite in the lowest oxidation state. Ilmenite crystallizes in the rhombohedral system and is typically long and lath-shaped.

11 Development of fine light-coloured ferri-rutile blades in ilmenite. The blades have grown in the {0112} and {0001} planes.

12 A heterogeneous intergrowth of bladed rutile and ferri-rutile in a titanohaematite-ilmenite host.

13 Sigmoidal (or leaf textured) rutile in titanohaematite, completely replacing the original ilmenite.

14 Pseudobrookite (grey) has now developed along the grain boundaries at the expense of the rutile-titanohaematite intergrowth.

15 Pseudobrookite with relic undigested haematite (bright blebs) and rutile (less bright elongated blebs) completely replacing the original ilmenite. This represents the highest oxidation state in ilmenite.

Figures 16–18 Low-temperature oxidation (maghaemitization) and replacement of titanomagnetite. Maghaemitization may take place either during late stages of the initial cooling (deuteric alteration) or perhaps during subsequent weathering.

16 Fine vermicular replacement of titanomagnetite (brown) by titanomaghaemite (lighter coloured). Note renewed growth along sharp upper edge after original crystal had become well formed.

17 More advanced replacement by titanomaghaemite than in figure 16. Titanomaghaemite is optically isotropic and has a cubic atomic structure. It may range from nearly white to a bright blue colour.

18 The bright area is totally maghaemitized. The cracks are typical at this stage. In the darker cracked area, the titanomaghaemite has been replaced by a fine granular, amorphous iron-titanium oxide.

Figures 19–21 The various forms and types of secondary oxides produced in altered olivine. These intergrowths are strongly magnetic and are associated with the highly oxidized titanomagnetite and ilmenite grains.

19 Subgraphic magnetite developed in altered olivine.

20 Gradational development of haematite towards the edge of an olivine crystal by iddingsitization.

21 Development of irregular haematite veinlets along cracks in an oxidized olivine grain.

the magnetic field. These can be separated by slow thermal demagnetization. Two such rocks have been found, each containing two different, and both reversed, magnetizations. No postulated self-reversal mechanism can account for this, while field reversal plus the known histories of the rocks can.

It has occasionally been found that a wide variety of rock types from one locality all have the same magnetic polarity. The variety makes it unlikely that all of them share the same reversing property (if all are reversed) or non-reversing property (if all are normal). Such a wide variety was found in the Tertiary rocks of Northern Ireland, and this particular group indicates field reversal, since they were all reversed.

In addition there are four known instances of time-ordered sequences of lavas that apparently record the change of the ancient magnetic field from one polarity to the other, with directionally intermediate steps. Self-reversal cannot explain the gradual swing of direction of magnetization from lava to lava. A more reasonable explanation is that these examples show field reversal 'caught in the act'.

Finally, it is found that the range and mean value of the ancient field-intensity that is deduced from normally magnetized rocks is the same as that deduced from reversely magnetized rocks. It is unlikely that a self-reversal mechanism would produce the same values as occur in normally magnetized rocks, and this suggests, again, that there has been a reversal of the earth's magnetic field. If this has occurred, the results show that there is no asymmetry between the two possible states of the field.

Self-reversal

In 1952, T. Nagata, S. Uyeda, and S. Akimoto discovered some lava specimens on Mt Haruna that would change their magnetic polarity if they were heated [1]. The magnetic fraction of the rock was investigated, and it was found the reversals were consistent and repeatable. As the rocks occur in nature with reversed polarity, it was suggested that these were examples of self-reversing rocks whose polarity had changed as they cooled. It was held, therefore, that reversed rocks might not represent reversals of the earth's magnetic field. However, the only other rock of this type so far discovered is a haematitic iron ore examined by C. M. Carmichael [2]. Ideally, the rocks chosen for palaeomagnetic studies are relatively common rocks that are laid down in a known orientation at a known time: basic lavas are ideal. Neither of the self-reversing rocks is of a type that is commonly used for these purposes—the first is comparatively rare, and it is not possible to establish the time of magnetization of the second. The rocks—such as basalt lavas—that are more usually studied for this purpose never show, in the laboratory, more than tendencies to reverse their polarity on heating, and that only rarely. Even in these rare cases, the variation of polarity on heating shows a very distinctive pattern that is quite different from that of most naturally occurring rocks of reversed polarity. The evidence for field reversal has convinced most workers that field reversals are a reality, and that self-reversal is extremely uncommon.

Although truly self-reversing rocks have been so rarely found, a lingering suspicion remains that self-reversals might have frequently occurred in some subtle way which the tests have not disclosed. The evidence for self-reversal might have actually vanished, but it seems reasonable to suppose that some evidence should have persisted in the reversed rocks, and should be missing in the normal ones. The hunt for differences between normal and reversed rocks began, naturally enough, with a search for magnetic differences. None could be found until recently, and no one could claim they are conclusive differences. However, the hunt for petrological or chemical differences has gradually accumulated evidence that the oxidation state is often higher in reversed lava specimens than in normal ones. The chemical evidence is that iron is in the high valency (Fe^{3+}) state more frequently in reversed rocks; and the petrological evidence is that the iron-titanium oxide crystals are visibly in different, more highly oxidized, crystal form, while some of the silicate minerals are noticeably more reddened. The figures show stages of

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progressive oxidation in the two common iron-titanium oxides in basalt lavas, namely titanomagnetites (figures 1–9 and 16–18) and ilmenites (figures 10–15). The ilmenites themselves contain a higher ratio of Fe_2O_3 to FeO than do the titanomagnetites; and there is sometimes a preponderance of ilmenite in reversed lavas that may also indicate higher oxidation states. Olevines in highly oxidized states also contain strongly magnetic material, which is easily seen beneath the microscope (figures 19–21).

Table 1 shows the evidence that has been gathered in the last few years. It is clear from the table that eight independent research teams or individuals have found chemical differences between normal and reversed lavas from thirteen different locations spread well over the earth's surface: the lavas are not confined to one geological period. The predominant difference reported is that of oxidation state.

It is interesting that many of the teams did not believe their own results to be significant. For example, A. L. Bol'shakov, G. M. Soldovnikov, and Yu. P. Skovorodkin found the Fe_2O_3/FeO ratio to be 4·2, on average, for reversed rock, and 1·2 for normal [3]. But since the two distributions of the ratio overlapped, and since they found evidence of the type earlier discussed for field reversal, they rejected the oxidation difference as accidental. In any single investigation, that is a reasonable attitude. However, in view of the total evidence, the oxidation difference must be taken much more seriously. Even so, the statistical nature of the evidence must be taken into account; although some normal specimens are highly oxidized and some reversed ones are not, these are exceptions to the statistical rule. For this reason, the authors have adopted the working hypothesis that the reversed rocks almost invariably represent real reversals of the earth's magnetic field polarity. If further investigation supports this proposal, the high and low oxidation states must then be associated with the reversed and normal states of the magnetic field. The crucial question is how this can be so.

The link between oxidation and reversal

We do not here suggest any mechanism to link oxidation state of the lavas with the polarity of the magnetic field in which they have cooled, but it is possible to indicate a few lines of reasonable investigation. One necessity is the accumulation of further evidence confirming a link, and an extension of the investigation to intrusive bodies which have not been in contact with the atmosphere during cooling. We can thus tell whether the oxidation state is inherent in the upwelling lava, or whether it is due to contact with the atmosphere, and this will narrow the field of hypotheses.

Further, the red sandstones must be examined from a similar point of view, using especially the Fe_2O_3/FeO ratio as a measure of oxidation state. As red sandstones have acquired their magnetization at ordinary temperatures, by a mechanism different from that of lavas, a new line of evidence may appear. It is known that red sandstones occur both normally and reversely magnetized.

Further, it must be kept in mind that the oxidation state, while easily recognizable, may not be the critical and illuminating parameter to correlate with magnetic polarity in a specimen. Perhaps we should look for another difference, loosely connected with oxidation state, but more closely related to magnetic polarity.

The point of interest now is that the totality of evidence seems to contain internal self-contradictions. Petrological, chemical, and slight magnetic differences suggest the past existence of self-reversal in lavas on a wide scale; while all other tests positively point to field reversal, denying self-reversal as a common phenomenon. In at least three lava sequences, widely separated in space and geological time, both kinds of evidence have been found in the same sequence of lavas. The only way to resolve the clash seems to be to assume that reversed rocks mean a reversed field, and that the oxidation state of the lavas is statistically associated with the field polarity. The problem then reduces to finding a mechanism that links oxidation states in lavas to the polarity of the magnetic field in which they cool, and it is at present possible only to make guesses at the nature of this mechanism.

Table I

Rock type and location	Nature of differences between normal and reversed specimens
Basalts in Germany	A difference of petrological texture [4].
Basalts in Germany	Differences of grain size and texture. Also differences in form of olivine grains [5].
Metamorphic rocks in the Adirondack mountains, United States	Reversed specimens more highly oxidized than normal specimens. Petrological and chemical analysis [6–8].
Angara basalt traps, Southern Siberia, Soviet Union	Reversed lavas have 1·36% TiO_2, normal have 0·83%. Also magnetic differences [9].
Basalt traps of Southern Siberia, Soviet Union	Excess of ilmenite and TiO_2 in reversed specimens. This means a higher oxidation state [10–12].
Ultrabasic rocks of the Maymecha–Kotuy region, Soviet Union	Chemical and mineralogical differences (unspecified in *Geophysical Abstracts* 199–241) [13].
Lavas of central Kazakhstan	Reversed specimens more highly oxidized than normal specimens [14].
Quaternary lavas of Armenia	Fe_2O_3/FeO ratio greater in reversed (4·2) than in normal (1·2). Also seen petrologically. Also excess MgO in reversed lavas [3].
Basalt lavas, Isle of Mull, Scotland	Reversed specimens more highly oxidized than normal, deduced from several types of petrological observation. Differences in olivine alteration (oxidation) [15–17].
Basalt lavas from Scotland, Japan, and Iceland	Petrological analysis. Reversed specimens more highly oxidized. Icelandic result not statistically significant in itself [18].
Columbia Plateau basalts, United States	Petrological analysis. Reversed specimens much more highly oxidized than normal. Magnetic differences also exist [19].

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The answer is worth pursuing if only to convince ourselves about the reality of reversals of the earth's magnetic field. The presently accepted mechanism for production of the earth's magnetic field is a system of motions in the liquid core of the earth which acts as a self-exciting dynamo. Complex dynamo systems are known to be unstable enough for reversals to occur. It would be convenient to have certain confirmation of the occurrence of real reversals of the magnetic field, as this would limit the number of alternative theories of field generation that have to be considered. In addition, there is some evidence from radio-astronomy that Jupiter's magnetic field has a sense that is the reverse, relative to the direction of rotation, to that of the earth; and many stars are known, from the Zeeman splitting of their spectral lines, to reverse their magnetic polarities in days, and even hours. The study of changes in the earth's magnetic field may well lead to an understanding of changes occurring in planets and stars.

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Book reviews

RESEARCH ORGANIZATIONS

The Organization of Research Establishments, *edited by Sir John Cockcroft. Pp. 275. Cambridge University Press. 1965. 63s.*

This is a most unusual book. It is a collection of essays by the directors of a selected number of research establishments, both large and small, with a predominance of Government owned or Government sponsored institutions. Presumably they have been selected in order to display the wide variety of patterns existing in this country, though there is also an article on the Bell Telephone Research Organization.

Official documents usually give a description of a laboratory, its organization, its expenditure, and an account of the results achieved. Such documents are often dull to read and do not reveal the very real problems that arise in creating and in managing a laboratory to make it a living and active entity. Sir John Cockcroft as editor has induced the writers to give a more personal description of the way they manage their affairs. In this field it is very easy to be stereotyped, to talk of consultations with others, delegation of authority, and encouraging the bright investigator; and the authors are sometimes tempted to write in this fashion. However, the attractive and valuable feature of the book is the description of how they think laboratories should be managed. It emerges on reading the book that there is no set pattern, for this depends on the age of the laboratory, on the nature of the work, and also on the general attitude of the organization to which the laboratory belongs. One striking fact is that the pattern of direction, as is usual, has had to be evolved to suit the job in hand. Much of the personalities of the writers appears in these articles and this is all to the good. Sir Edward Bullard attempts the difficult job of summarizing the situation. The book can be very profitably read by a wide variety of scientists, particularly those who have the problem of looking critically at the management and the financing of scientific laboratories. *H. Melville*

COMPUTERS

Numerical Methods and Computers, *by Shan S. Kuo. Pp. x+341. Addison-Wesley, Reading, Mass. 1965. 59s.*

This is one of several recent books that illustrate some of the methods of numerical analysis and algebra with the aid of computer programs written in one of the high-level languages, usually ALGOL or (as in this case) FORTRAN. The language itself (more particularly the variant used on the IBM 1620/22 computers) is explained in Part I (nearly one quarter of the book). This section also describes the main features of a computer and the operation of a computer centre.

Part II describes computer-oriented numerical methods for the following:—solving polynomials and more general equations (in a single variable); step-by-step integration of differential equations (by the Runge-Kutta-Gill methods); problems of matrix algebra (inversion and determination of eigenvalues—symmetric case); interpolation and least squares fitting (including the use of Chebyshev polynomials); and Gaussian quadrature. This part concludes with a few words on the subject of errors, mainly distinguishing between round-off error and truncation error.

Part III gives an introduction to the 'Monte Carlo' technique of random sampling to evaluate the properties of a system, and it also gives some of the methods of linear programming.

Three appendices deal with (1) operating the IBM 1620/22 computers, (2) conversion to and from the binary number system, and (3) a proof referred to in the text.

The text is largely taken up with programmed examples and discussion of results of actual machine runs. As a consequence the topics covered are explained well, but otherwise the treatment is fairly elementary. On the other hand, space is not wasted by a description of outdated methods. There are many exercises and a good bibliography at the end of each chapter. *R. A. Brooker*

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COSMOLOGY

The Measure of the Universe, a History of Modern Cosmology *by J. D. North. Pp. xxviii+436. Clarendon Press, Oxford: Oxford University Press, London. 1965. 70s.*

This book comes at a most opportune moment. Cosmology, as a result of recent experimental information, gives every sign of being about to develop at a much greater pace. The most modern theories are too new for a writer to describe them with any perspective, but they have developed out of earlier theories, and can be understood only by first understanding cosmology as it has developed in the first half of this century. This is just the period selected by the author, and he describes it most delightfully. The first part of the book deals with various theories of cosmology. Those of the nineteenth century are summarized, and this is followed by an account of the difficulties in Newtonian theory which led to general relativity. There are then chapters on the expanding universe, on Milne's cosmology and related topics, and a description of the steady-state theory. The second part of the book considers philosophical questions such as the uniqueness of the universe, the status of cosmological principles and the question of infinities.

The whole provides a most illuminating and enjoyable introduction to the subject, with a minimum of mathematics and no demand for previous technical knowledge on the part of the reader.

C. W. Kilmister

SOLID-STATE PHYSICS

Fluctuation Phenomena in Solids, *edited by R. E. Burgess. Pp. xi+389. Academic Press, New York. 1965. 100s.*

The book contains eight chapters of varied length by different authors. Two long articles, on critical fluctuations by A. Münster, and on fluctuations due to electronic transitions and transport by K. M. van Vliet and J. R. Fassett, together make up nearly half the book. Some of the shorter chapters are too condensed to do justice to their material, though this is largely remedied by clear presentation and extensive bibliographies. Good indexes of authors and subjects are provided at the end of the book. The chapter by N. G. van Kampen on fluctuations in non-linear systems is particularly illuminating and instructive.

Although the various articles are legitimately brought under one title, they remain essentially separate, and the reader must bridge the gaps between them by his own labours. The field is already too large to be reasonably covered in one book, and the omissions in this volume emphasize this. Even so, it is a pity that the editor did not himself provide a connecting initial or final chapter. As it is, the book is far from an introductory text, though physicists and engineers with some experience in the general field of electronic fluctuations will read it with profit and a good deal of pleasure.

G. Wyllie

MICROWAVE SPECTROSCOPY

Microwave Spectroscopy of Gases, *by T. M. Sugden and C. N. Kenney. Pp. ix+332. D. Van Nostrand Company, London. 1965. Cloth, 70s.; paper, 35s.*

After twenty years of development, microwave spectroscopy has for some time been well enough established to merit treatment in monographs intended for advanced undergraduate study and for use by research workers and others not necessarily specialized in the field. As such a work, this survey is therefore timely. Although their treatment is not comprehensive, the authors have wisely decided that some guidance through the derivation of the main mathematical formulation is essential to a proper understanding of the field, and they make their approach very directly through quite detailed discussion of the quantum theory of rotating bodies. By using the rigid diatomic molecule for basic discussion and elaborating the treatment as justified by more complex cases, they should convince much of their readership that a reasonable grasp of the mathematical principles of rotation spectroscopy is within its capability. By means of intelligent selection and use of mathematical appendices, a treatment is provided which cannot fail to be valuable to advanced students in both chemistry and physics.

The experimental methods, placed rather late, are described readably and adequately, perhaps less than full advantage being taken of the fascination of their powers of resolution and sensitivity. In the illustration of results, there are some variations in emphasis which, in part, mirror the authors' particular experience. Thus there are fairly long treatments of symmetry effects due to identical nuclei, of nuclear spin effects and of Stark effects. In contrast, the now very large field of accurate determinations of molecular geometry is scarcely treated in sufficient detail, except in a 68-page bibliography of somewhat limited value.

With this exception, however, the work fulfils its aim very well, and is a valuable addition to the literature of a subject too much neglected in Great Britain.

J. Sheridan

LUMINESCENCE

Luminescence—L'électron et la lumière, Matière et photoluminescence, *by G. Monod-Herzen. Pp. viii+288. Dunod, Paris. 1966. 39F.*

This is a book in two main parts. The first part attempts to present topics which are said to be inadequately covered in the usual textbooks of optics. This may be true in France, but a physics undergraduate in England will certainly have met all of the topics covered in a more quantitative and less descriptive way than in the treatment given in the present text.

The second part has a similar fault of being too descriptive, and is also uncritical. The section on luminescence in crystals is already better covered from the same publisher by Daniel Curie's recent book 'Luminescence in Crystals'. The section on gases and vapours is much too superficial, and the reader would be advised to go direct to a more specialized book such as Pringsheim's 'Fluorescence and Phosphorescence'. The reader is given no proper references to the literature, although Pringsheim is referred to for a bibliographic review (it was published in 1946!). Reference is made to three books published in France (only one is of recent origin), but no reference to that by Daniel Curie, perhaps because his monograph, which exists in an English translation, makes the present volume superfluous. It is difficult to see that M. Monod-Herzen's text fulfils any need among undergraduate or graduate readers here. The latter would certainly demand a more substantial introduction to luminescence.

G. F. J. Garlick

PHYSICAL CONSTANTS

Tables de constantes et données numériques. Constantes sélectionnées — Pouvoir rotatoire naturel — *Vol. 1a,* Steroids, *by J. Jacques, H. Kagan, and G. Ourisson. Second edition. Pp. xxx+1031. Pergamon Press, Oxford. 1965. £18 10s.*

This book brings up to date an earlier catalogue of the optical rotations of steroids published in 1956. Although large and expensive, it is essential for all laboratories working in the steroid field—and highly desirable for other laboratories which are interested in the general relations between optical rotation and structure. The literature is covered up to 1961, structures being corrected up to 1964 where necessary. About 21 000 compounds are listed, in contrast to the 8000 compounds in the previous edition.

The introduction, in both French and English, deals with the nomenclature of steroids. The compounds are catalogued

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under their molecular formulae with full references (6300 in all); the book includes extremely thorough indexes to authors and substances. References to the important new technique of optical rotatory dispersion are given briefly.

Since optical rotation values are given for nearly all new steroids, this book really constitutes a one-volume catalogue of steroids; this is therefore the easiest place in which to begin a literature search. The French authors are to be sincerely congratulated on carrying forward the good work of the first edition.

W. Klyne

SURFACE SCIENCE

Semiconductor Surfaces, *by A. Many, Y. Goldstein, and N. B. Grover. Pp. xvi+496. North-Holland Publishing Company, Amsterdam. 1965. £5 10s.*

The transistor effect which still dominates solid-state electronics was discovered seventeen years ago by Bardeen, Brattain, and Shockley while investigating germanium surfaces. This was perhaps an accident, but it illustrates the significance of surface science in the semiconductor field. The interest in surfaces is now rapidly increasing, and a review of semiconductor surface studies is therefore timely.

The authors have produced an account that is a joy to read, sufficiently simple to appeal to a wide circle of solid-state scientists, and at the same time as impeccably learned as a treatise can be. Three introductory chapters provide a brilliant, brief survey of the situation, a text on bulk semiconductor physics for the ignorant, but very bright, or perhaps those requiring a refresher course, and an excellent account of the different aspects of surface research. This introduction is followed by two theoretical chapters on the space-charge region and on surface states, and two chapters in which the experimental methods are described and analysed. Thus a basis is prepared for the two final chapters in which all information available about germanium and silicon surfaces is critically reviewed and laid before the reader. Only occasionally is reference made to other materials, such as cadmium sulphide. Engineering aspects are not included in the discussion.

The usefulness of the book is increased by about 800 well-ordered references, two extensive indexes, and a list of symbols.

W. Ehrenberg

Recent Progress in Surface Science, *Vols. I and II, edited by J. F. Danielli, K. G. A. Pankhurst, and A. C. Riddiford. Pp. xii+414; xiii+541. Academic Press, New York. 1964. 114s.; 128s. 6d.*

This new serial publication will publish reviews summarizing the rapid advances being made in all branches of surface science. The first two volumes have been published simultaneously.

Volume I begins with a review on surface viscosity by M. Joly. There follows an excellent article by J. A. Kitchener on foams and free liquid films, which includes an account of recent work both on black soap films and on microfilms. D. A. Haydon's review on the electrical double layer and electrokinetic phenomena selects for special consideration the theory of the double layer and the electrophoresis of large particles. 'Electrode processes' by S. Schuldiner deals with modern measurement techniques and with electrochemical kinetic theory, and includes a discussion of the electrolytic hydrogen reaction. The problem of the corrosion of metals in aqueous media is reviewed by C. V. King, and W. A. Black gives a picture of the development of new surface-active agents, as seen by an industrial research worker. The next chapter, by E. Tannenbaum Handelman, on the chemistry of the semiconductor surface, includes sections on atomically clean germanium and silicon surfaces, and on compound and organic semiconductors. W. D. Stein writes on facilitated diffusion across membrane surfaces. He concludes: 'We have no clear idea of the mechanism of action of facilitated diffusion'. The problem of cell contacts is reviewed by E. J. Ambrose. E. H. Mercer's chapter on the external surface of the cell and intercellular adhesion takes up and elaborates some of the topics dealt with in the previous chapter. The final chapter on formation and properties of bimolecular lipid membranes, by P. Mueller, D. O. Rudin, H. Ti Tien, and W. C. Westcott, is more of a research paper than a review.

In Volume II, M. M. Dubinin, B. P. Bering, and V. V. Serpinskii give a valuable review of physical adsorption at the gas-solid interface. The next chapter, a somewhat gloomy one by D. Brennan on heterogeneous catalysis, restricts attention to a few simple reactions. He concludes that 'it is unfortunate that, in a field which has attracted so much effort, . . . there should still be no basic hypothesis to describe the catalytic behaviour of surfaces, even for the simpler systems'. The subject of contact angles, reviewed by G. E. P. Elliott and A. C. Riddiford, has sprung into prominence again recently. J. T. Davies's contribution on emulsions should be one of the most useful chapters of the book. The longest chapter comes from A. S. Joy and A. J. Robinson on flotation. Both the industrial empiricisms and the very incomplete theory of flotation are discussed. Another long chapter is written by G. H. Beale on the genetic control of cell surfaces. The remarkable physiology of pinocytosis ('cell-drinking') is described by R. C. Rustad. An equally fascinating chapter is written on plastron respiration by D. J. Crisp. The volume concludes with two chapters on cell surfaces which are complementary to similar chapters in volume I. That by C. H. O'Neill discusses the preparation and properties of isolated cell surface membranes, while P. F. Elbers writes on the image and interpretation of the cell membrane.

These two volumes appear to hold promise of a very valuable series.

D. H. Everett

PHYSICAL CHEMISTRY

Acid-Base Equilibria, *by Edward J. King. Topic 15, Vol. IV of* The International Encyclopedia of Physical Chemistry and Chemical Physics. *Pp. xi+341. Pergamon Press, Oxford. 1965. £6.*

This is a well-planned and well-written book. Almost half is devoted to methods of measuring acidity constants. This provides, for the reader, a firm connection between the theoretical development and imaginable experiments. The influence on acid-base equilibria of molecular structure, of temperature and pressure, and of species not directly involved in the equilibria, are then considered in separate chapters. An introduction to the biologically important field of polyelectrolyte acid-base equilibria is also included. Finally, there is one chapter on non-aqueous systems and one on the general question of the acidity of solutions.

Although an elementary knowledge of thermodynamics and of electrolyte theory is assumed, this work should prove useful to physical chemists interested in the subject as such, and also to others—such as biochemists—who may want to deepen their understanding of the concept of acidity.

The series seems as if it will be more like a small library than the usual idea of an encyclopedia: this book, at least, is a quite straightforward textbook, with a full and up to date bibliography.

A. G. Cairns-Smith

ELECTROCHEMISTRY

Oscillometry and Conductometry, *by E. Pungor (translated from the Hungarian by T. Damokos and edited by A. Townshend). Pp. xvi+239. Pergamon Press, Oxford. 1965. 70s.*

There has been no single volume devoted to conductometry since Britton's text of

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1934, which has been long out of print, and high-frequency methods are served only by Blake's early monograph and Oehme's short text in German. This collected account of low-frequency and high-frequency methods is therefore timely. The two methods are not segregated in the text, but rather treated side by side, which emphasizes their similarities and is in accordance with modern views. The text is divided into five parts, covering the fundamentals of low and high frequency conductance measurements and the measurement of dielectric constants; instrumentation and cells for the three types of measurement; acid-base reactions; precipitation complexation and electron transfer reactions; and other applications such as kinetics and water determination. The bibliography extends only as far as 1961, but it includes nearly all the earlier work. This book offers an accurate and satisfactory introduction to the subject, but except in one or two topics, particularly those concerning the author's own instrument, the treatment is not adequate for the full understanding of the principles, the practical interpretation and construction of the circuits, or the operation of the instruments without reference to the original papers. Translation, indexing, and production are good. *E. Bishop*

SOLID-STATE CHEMISTRY

Progress in Solid State Chemistry, *Vol. 2, edited by H. Reiss. Pp. viii+471. Pergamon Press, Oxford. 1965. £6.*

In the preface the editor states that this work aims to present topics 'in a manner intelligible to both chemists and physicists'. Provided that these chemists and physicists are able to approach the subject matter with a general background knowledge of the solid state in relation to crystal structures, band theory, and lattice imperfections, that aim has been largely fulfilled. There are twelve articles, and whereas volume 1 emphasized strongly the structural aspects of the subject, the present collection has a better balance, in that kinetics and reactivity also receive attention, albeit still a minor attention.

Several of the articles are reviews, including two excellent comprehensive accounts of low-energy electron diffraction by J. J. Lander and non-stoichiometry by G. G. Libowitz. Three chapters cover aspects of nucleation and precipitation, and one, by L. Kevan, is a descriptive account of the reactions of radiation-produced electrons. Other articles, by F. Hulliger and E. Mooser, and by H. Schmalzried, centre closely about the authors' own researches, and are interestingly written as well as being authoritative. M. F. C. Ladd and W. H. Lee continue from volume 1 their useful compilation of lattice energies.

The book is well produced and it fills a useful function, but the editor and publishers could improve the usefulness of these volumes if they made more thorough subject indexes, perhaps by asking their authors to suggest entries.

F. S. Stone

ACETYLENE

Acetylene, Manufacture and Uses, *by D. W. F. Hardie. Pp. xii+102. Oxford University Press, London. 1965. 16s.*

This series for senior students in schools and junior students in colleges and universities is intended 'to give a practical dimension to theoretical instruction'. The sixth in the series, 'Acetylene', is well up to its predecessors in the excellence of the production and in the interest and relevance of the contents. Dr Hardie shows how the structure of acetylene is responsible for its important role as a bridge between inorganic materials and carbon compounds of great diversity. He describes the manufacture of acetylene both from lime and coke via calcium carbide, and from methane and other hydrocarbons, and then outlines its uses in synthetic industrial chemistry for making vinyl chloride, neoprene, and other chemicals. There is an interesting chapter outlining the historical development of acetylene as a substance of industrial importance. The book gives the student a readable and up to date account of its subject.

The whole of this series of books is useful in enabling the student to see how the fairly simple academic chemistry he learns about is relevant and important in the world outside the classroom; and to realize that it is the basis on which the chemical industry, in which so many students will find their livelihood, is built.

G. Van Praagh

METALLOCENES

Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene, *Part I, by Myron Rosenblum. Pp. xv+241. Interscience Publishers, London. 1965. 95s.*

The publishers promise us a series of monographs in the field of organometallic chemistry under the editorship of Professor Dietmar Seyferth. This book is the first part of a two-volume set that introduces the series, and the list of pending titles and authors looks impressive. If the high standard set by Dr Rosenblum is maintained, they will be useful works.

The present volume has six chapters—preparation of metallocenes, electronic structure and bonding, physical properties, acylmetallocenes, alkylmetallocenes, and arylmetallocenes—and is the most comprehensive review of this field to date. The first three chapters are of general interest, giving a comprehensive cover of the various synthetic methods available for these compounds, an account of the various bonding theories, and finally a description of the very wide diversity of physical methods that have been used in the study of the metallocenes. The last three chapters (representing over 70 per cent of the contents) are concerned mainly with the extensive organic chemistry that has now grown up around the ferrocene nucleus. The reviewer was not overfamiliar with this latter aspect of metallocene chemistry and was pleasantly surprised at its interest.

There is extensive use of structural diagrams and tables, and the literature is reviewed to the end of 1963. *E. W. Abel*

ALKALOIDS

The Isoquinoline Alkaloids, a Course in Organic Chemistry, *by K. W. Bentley. Pp. vii+264. Pergamon Press, Oxford. 1965. 25s.*

This is an admirable short monograph covering the isoquinoline, benzylisoquinoline, bis-benzylisoquinoline, apomorphine, morphine, berberine, phthalideisoquinoline, and emetine groups of alkaloids in a clear and authoritative manner. There is also a short addendum on the biogenesis of these various types. The chapter on the morphine alkaloids, a subject on which the author is an established authority, is particularly well done. This reasonably priced book will be most useful to third-year university students who want a concise and critical account of one of the most important groups of alkaloids. In a book of this scope, references to original papers are rightly not given, but it is a pity that a few references to leading review articles are not cited.

A minor error was noted on page 253. Robinson and Schöpf independently discovered the oxidative cyclization of laudanosoline (not norlaudanosine as stated): the similar reaction of norlaudanosoline (No. 57 on page 254) was in fact first performed much later by the present reviewer using a different reagent, and the product (No. 58 on page 254) is incorrectly formulated.

J. Harley-Mason

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PHYSICAL GEOLOGY

Principles of Physical Geology, *by Arthur Holmes. Second edition. Pp. xv+1288. Thomas Nelson & Sons, Edinburgh. 1965. 84s.*

The first edition of Holmes's 'Physical Geology' came as a welcome breeze of fresh air to enliven the somewhat stuffy atmosphere in physical geology at that time. It soon achieved great popularity—even to the extent of being very favourably reviewed in the Sunday press. This second edition has all the merits of the original—its modernity of outlook, its lucid and lively presentation of the subject, and its wealth of remarkable illustrations. But this new edition is almost a new book, two to three times as large as the first, and with yet more and still better illustrations. Not only have the old chapters been thoroughly revised but many additional chapters have been added that embody the application of recent advances in physics to the problems of geology. Recent results in the radiometric dating of minerals and rocks, the bearing of palaeomagnetism and palaeoclimatology on the movement of continental masses, the role of deep-seated convection currents in promoting crustal events, and the possibility and consequences of an expanding Earth are a few of the many topics explored. If anyone wants to know what modern physical geology is all about, here is his answer.

H. H. Read

NEUROPHYSIOLOGY

Elements of Neurophysiology, *by Sidney Ochs. Pp. vii+621. John Wiley & Sons, London. 1965. 105s.*

During the last 40 years, and particularly in the last 15, the advances in knowledge of the nervous system have been very great. This advance has partly resulted from the wide application of electronic techniques in such studies and from the advent of the electron microscope, but the wide interest in nervous systems and their physical imitation in calculators and the devices of automation have also played a part. The present book gives a well-balanced account of many recent advances with a background of classical physiology; it is a valuable guide to the advanced student in this field, where the sheer bulk of recent references makes it difficult for him to follow original sources. A straightforward account is given of almost the whole field of neurophysiology, and while the account assumes little background from the reader, it takes him right up to the most recent advances.

It has many illustrations selected from original authors and a bibliography to each chapter. The writing is clear and concise, and the whole can be recommended both to advanced students and to those in other disciplines who are interested in learning about the most remarkable instruments known to us, the brains and nervous systems of men and animals.

B. Matthews

SENSORY PHYSIOLOGY

Contributions to Sensory Physiology, *Vol. I, edited by William D. Neff. Pp. x+274. Academic Press, New York. 1965. 60s.*

This book is the first of a projected series which seems likely, if the standard so far set can be maintained, to be an important addition to the literature of the field. The object of the series is to provide a place for articles which can give a rather more extended account of a piece of recent research than is usually possible in a single paper, and yet yield a more coherent result than is obtained by the reader in wading through a series of such papers—the usual aftermath of reading a review. Such a role seems up to now to have been filled largely by the publication of 'symposia'. The superiority of these present accounts over the normal belatedly published resurrections of verbal presentations is striking.

This volume contains five articles on the special senses: the first two chapters give a finely illustrated account of current knowledge of the functional anatomy of the receptors and associated structures of the organ of Corti and the vestibular and lateral line organs. Then follows a very full treatment of the psycho-physiology of vestibular function, and finally there are two chapters on vision, the first an account of parallel electrophysiological and behavioural studies of colour vision, and the second an up to date essay on the very old problem of flicker fusion.

I. C. Whitfield

RADIOBIOLOGY

Unterlagen zur Neutronenbiologie des menschlichen Körpers, *by H. Schreiber. Pp. vi+91. F. K. Schattauer-Verlag, Stuttgart. 1965. 29DM.*

The increasing industrial applications of nuclear energy and the necessary study of neutrons in the research laboratory have naturally led to a growing interest in the possible biological consequences of exposure to these particles, of which the catastrophic effects of the first atomic bombs have made mankind only too aware. A book setting out these possibilities against a background of known experimental information could be very welcome. The '*Unterlagen*' referred to in this one, however, are very physical ones: the book contains no reference at all to specific biological changes. It forms a condensed review of recent 'physical' literature and is divided into four sections. The first deals with the physics of neutrons, of nuclear reactions, and of fission. The second considers the 'International Standard Man', discussing the I.C.R.P. (1955) data in the light of more recent physiological investigation; and the third, the chemical analysis of the more important human organs and tissues. Finally, the possible interactions of neutrons, over a wide range of energies, with the principal chemical elements forming these tissues are discussed and tabulated. The chief value of this book is therefore to radiobiologists who will find its elaborate and comprehensive tables and the literature references useful.

C. B. Allsopp

NUTRITIONAL BIOCHEMISTRY

Newer Methods of Nutritional Biochemistry, with Applications and Interpretations, *Vol. II, edited by Anthony A. Albanese. Pp. xiii+558. Academic Press, New York. 1965. 148s.*

This volume contains ten new essays by twelve authors, and in addition the editor writes a short epilogue on enzyme adaptation that is in effect another essay. Between them, the essays cover a very wide range of subjects in very different ways. Some do describe methods, such as those for the determination of fat-soluble vitamins. Some give a detailed theoretical account as a basis for a discussion of methods; the most readable chapter, by Passmore and Dreper on energy metabolism, is of this sort. Others are essentially a description of theoretical biochemistry of some significance to the nutritionist, but with little or no methodology.

Every chapter makes a useful summary of knowledge. It is, however, difficult to imagine that there are many whose interests are so wide, or knowledge so profound, that they would find all, or even most, of the chapters really worth studying. And it is difficult therefore to imagine why it is thought worth while to put together in one book such a diversity of writings.

J. Yudkin

NUCLEIC ACIDS

Progress in Nucleic Acid Research and Molecular Biology, *Vol. III, edited by J. N. Davidson and Waldo E. Cohn. Pp. xiv+363. Academic Press, New York. 1964. $11.50.*

Today the study of nucleic acid structure and function, by every possible technique available, engages the attention of large numbers of the world's best scientists. Discoveries come so rapidly that it is

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difficult for the non-specialist to keep up to date, except by progress reports, such as these.

All the articles make fascinating reading, and some of them have a specialist appeal. Thus the chapter on the isolation and fractionation of nucleic acids by K. S. Kirby is extremely valuable to newcomers to the field. Joseph Weiss has produced a brilliant and comprehensive article on chemical effects of ionizing radiations on nucleic acid and related compounds. P. Mandel's chapter on free nucleotides in animal tissues is timely and important. All the articles contain excellent references, and the author and subject indexes at the end of the book are very valuable.

As with all the books from this particular publisher, the diagrams are beautifully produced and the arrangement and printing are excellent.

These volumes are essential for all workers interested in nucleic acids and their associated macromolecules.

M. Stacey

ANIMAL NUTRITION

Nutrition animale, *Vol. III*, Données générales sur la nutrition et l'alimentation, *by R. Jacquot, H. le Bars, A. M. Leroy, and H. Simonnet. Pp. 1431–2179. J.-B. Baillière et Fils, Paris. 1964. 82,45F.*

The *Nouvelle encyclopédie agricole* is to include a comprehensive account of animal nutrition in ten volumes. This third volume is of particular interest, for it deals with subjects of general importance —food intake, digestibility, metabolic pathways, nutritional requirements, and feeding standards. It is like its predecessors in the clarity of its exposition and its admirable thoroughness in going from basic principle to practical application.

This volume begins with a detailed consideration of the manner in which the intake of food may be controlled in the various species. An extensive discussion of protein metabolism follows—something to be expected from those close to Terroine's work—with the complex problems of rationing clearly set out. Surprisingly, consideration of the energy-producing component of the diet is not considered until the vitamins have been fully discussed. In what is obviously intended to be a standard work on the subject, it is regrettable that so much of the important work by nutritionists in Australasia and Great Britain which is leading to modification of accepted feeding standards in ruminants is largely unnoticed. Almost nothing published after 1961 is considered, while the list of references as footnotes represents a small proportion of the authors named. The final section on mineral requirements maintains a high standard of comprehensiveness and clarity.

T. K. Ewer

PLANT ECOLOGY

Forest and Savanna, an Introduction to Tropical Plant Ecology, with Special Reference to West Africa, *by Brian Hopkins. Pp. xii+100. Heinemann, London. 1965. 18s.*

Students of botany, agriculture, forestry, geography, and indeed anyone interested in vegetation and land use in the tropics will be grateful to Dr Hopkins for this book. There has long been a need for a short and inexpensive textbook that described the principles and methods of modern plant ecology in terms of tropical vegetation. The author does this admirably, even though attention is confined to a rather small sample of vegetation types. It has been written primarily for students in English-speaking West African countries, but it deserves a place also in British and North American schools and universities, where ecology is all too often taught exclusively in terms of temperate vegetation.

An account of the different types of West African forest and savanna occupies most of the text. Distribution, structure, physiognomy, floristic composition, and ecological factors are systematically described, and in a judicious discussion of the forest-savanna boundary, Dr Hopkins concludes that there was no pure grass savanna in West Africa before man began to destroy the natural cover of forest and woodland. The value of this little book is enhanced by appendices on field methods of vegetation analysis and on student projects.

D. R. Harris

PLANT TAXONOMY

The Identification of Flowering Plant Families, including a Key to those Native and Cultivated in North Temperate Regions, *by P. H. Davis and J. Cullen. Pp. 122. Oliver and Boyd, Edinburgh. 1965. 12s. 6d.*

There has long been a need for a compact guide to the commonly encountered families of flowering plants, and that need is now met by this book. The main body of the text consists of dichotomous keys for the identification of all Angiosperm families, whether they be native or cultivated, out of doors or under glass, in North Temperate Regions. The keys are preceded by a refreshingly clear discussion of 'fusion' of floral parts, and of the various types of placentation, and are followed by terse descriptions of the families, a useful list of books for further identification, and a glossary.

The keys seem to work well, with clear and practical dichotomies. Apart from its use for identification, this book will be welcomed as a handy summary of family characters by teachers and students. Perhaps in a future edition room could be found for brief descriptions of a number of important or taxonomically interesting tropical families. A student living in the North Temperate zones is as likely to be interested in the Burmanniaceae or Dipterocarpaceae as in Epacridaceae or Xyridaceae—though thanks to the authors, he can now look up the latter in a book that will actually go in the pocket.

M. C. F. Proctor

ASPERGILLUS

The Genus *Aspergillus, by K. B. Raper and D. I. Fennell. Pp. viii+686. E. & S. Livingstone, Edinburgh; The Williams and Wilkins Co., Baltimore. 1965. £8.*

This work is an extensively revised and expanded version of Thom and Raper's 'Manual of the Aspergilli', published in 1945. An additional 55 species are recognised in the present volume and the 150 species and varieties are classified into eighteen Groups, mainly on the basis of morphology and pigmentation as defined previously in the Manual. Many specific names are reduced to synonyms. Several ascosporic species have been discovered since 1945 and are now correctly termed cleistothecial stages. The greatly increased number of illustrations are of excellent quality, and although the colour plates have been omitted from this revised volume without detriment, Ridgway's colour standards remain essential for its accurate use in identification. Although the book retains as its prime purpose the identification of Aspergilli, it is made more comprehensive by covering much biochemical, physiological, and genetical data accumulated during the intervening twenty years. Discussion of variation in the genus now encompasses heterokaryosis and parasexuality. Due recognition is given to the prominence of *Aspergillus nidulans* in microbial genetics, and the closely related *A. heterothallicus* (sp. nov.) is noteworthy because it is the first member of the genus in which heterothallism has been verified. Furthermore, the considerable medical and veterinary importance of Aspergilli has led to the inclusion of a chapter on pathogenicity contributed by P. K. C. Austwick. This beautifully produced, authoritative work will be indispensable to all those working with this group of fungi and is appropriately dedicated to the memory of Charles Thom.

A. T. Bull

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ARTHROPODS

The Behaviour of Arthropods, *by J. D. Carthy. Pp. vii+148. Oliver and Boyd, Edinburgh. 1965. Cloth 21s.; paper, 12s. 6d.*

This book is the first in a new series of university reviews in biology. A surprising amount of information is provided in its 148 pages, much of it from recent work. It ranges over many aspects of the subject, including, for example, the effect of endocrine organs and pheromones on behaviour. The book is so arranged that the subject is considered mainly under various activities of the animal, such as feeding, host finding, courtship and mating, social life, and migration, and this arrangement makes it of interest to invertebrate zoologists. Other chapters include work on the arthropod nervous system, posture and rhythms: the final one discusses inherited and learnt behaviour, and briefly touches on the possible evolution of certain patterns.

The condensation necessary to include so much material has made some parts a little difficult to understand, and it is likely that a few diagrams will not be fully understood from the text and captions. One wonders if some omission of material and rather more explanation of the remainder would not have been advantageous from the point of view of students. However, as a brief survey of a fascinating subject, it is undoubtedly a most useful volume. *J. G. Thomas*

NEMATODES

The Physiology of Nematodes, *by D. L. Lee. Pp. x+154. Oliver and Boyd, Edinburgh. 1965. Cloth, 21s.; paper, 12s. 6d.*

This inexpensive book will be welcomed by those wishing there was more interest in the roundworms themselves rather than in the havoc they cause. Its importance is that it cuts across the boundaries which too often separate nematologists in the different fields of animal and plant pathology.

Dr Lee's seven chapters summarize recent work on alimentary physiology, metabolism, osmoregulation and excretion, growth processes, neurophysiology, and behaviour. An introduction to nematode morphology and an appendix of abbreviated life cycles cater for the needs of the uninitiated.

Tyros will be disappointed if they expect all to be explained in this short work. The defects are sometimes a consequence of its shortness; rarely the fault of the author; and usually a measure of the inadequacy of our knowledge of practically every aspect of nematode physiology. Although there is certainly enough information in support of Dr. Lee's claim that all nematodes are not like *Ascaris*, comparative data are particularly lacking, and this is perhaps where attempts at a synthesis such as this are most valuable. Gaps in a table may well stimulate someone somewhere to set about filling them. *P. A. G. Wilson*

OCEANOGRAPHY

Serial Atlas of the Marine Environment. *Folio 8,* Zooplankton Indicator Species in the North Sea, *by J. H. Fraser;* The Trace Elements, *by R. Johnston. Folio 9,* Meteorology of the North Sea, *by F. E. Lumb. Folio 11,* Inorganic Nutrients in the North Sea, *by R. Johnston and P. G. W. Jones. American Geographical Society, New York. 1965. Bound, $6; $6; $7.50. Loose-leaf, $4; $4; $4.50.*

The first of these works gives a selection of zooplankton species, regarded as typical of eight chosen areas characterized by water type, and then deals with some of the oceanic organisms that come in from the north and have been found within the North Sea, that is, south of 61°N. The author draws largely upon information either already published by himself or held in his files at Aberdeen. In a chart of particular interest he delimits the apparent southerly reach of oceanic species in most of the years from 1920 to 1963, and we see that 1946 was the year of furthest penetration and 1937 that of least. To this valuable study are appended three clear charts—one showing the distribution of the species of Sagitta which excel as indicator organisms. An appended footnote tells about the plankton atlas being published in serial parts in the (Hull) Bulletins of Marine Ecology.

Because the production of an atlas portraying trace element occurrence in the North Sea alone would necessarily be based on very scanty data, Johnson, in the second study, extends his attention not only to the adjacent waters but to a very much wider background. We read that the older analyses which related to the North Sea and the English Channel tend to show an illusory richness when compared with modern analyses. Thirty-four trace elements are considered with reference to their occurrence in the seas and oceans at large, and the two charts presented contrive by means of very ingenious symbols to convey the distribution of presently-held information to which future data for the North Sea can be conveniently added.

Lumb's excellent study deals with atmospheric pressure, winds, fog frequency, air temperature, gales, cloudiness, and climatic variability. It includes seven figures and nine plates. A very useful feature of this study is the portrayal in clear charts of the air temperature extremes which march with atmospheric pressure extremes.

In the last of the works, the authors deal with inorganic phosporus, nitrogen, and silicon; with nitrite; and with phosphorus compounds in their free, dissolved, and particulate forms. They remark that richness in nutrients can, in general, be traced to the influx of oceanic water over the northern part of the North Sea, but in the southern part is attributable to the land drainage, sewage, and industrial effluents contributed by the large inflowing rivers. Most of the information presented in the ten full-page plates comes from investigations made by the Lowestoft and Aberdeen laboratories, but data from stated continental sources are also used. *J. N. Carruthers*

MICROBIOLOGY

Medical Microbiology, a Guide to the Laboratory Diagnosis and Control of Infection, *edited by Robert Cruickshank. Eleventh edition. Pp. xi+1067. E. & S. Livingstone, Edinburgh. 1965. 55s.*

This new title disguises 'Mackie and McCartney', familiar to all bench workers in medical microbiology; the book is much enlarged, and there are now eleven contributors. The new edition is intended to be an all-purpose textbook of microbiology, and with this aim in view, the sections on general topics have been considerably expanded. However, those who have found previous editions invaluable as a source of information on practical procedures will be glad to know that the present version has lost none of its usefulness, and that the technical sections have been enlarged and brought up to date. Additions to the sections on applied microbiology and techniques include biochemical tests used in identification of bacteria, care of experimental animals, and laboratory diagnosis of common infective syndromes. The general sections now provide a useful, though in some respects incomplete, background on which knowledge of practical procedures may be based. For example, there are excellent sections on bacterial anatomy and bacterial genetics, but there is a surprising dearth of information about antibiotics. Virology is generously dealt with in several sections of the book, which provides an admirable résumé of the subject. There are useful lists of references at the end of each chapter.

S. E. Reed

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TOXICOLOGY

Progress in Chemical Toxicology, *Vol. II edited by Abraham Stolman. Pp. x+416. Academic Press, New York. 1965. 100s.*

The first chapter of this volume deals with the absorption, distribution, and excretion of nearly 200 compounds, which include gases and vapours, volatile liquids, and various drugs, insecticides, and metallic poisons. Many of these compounds have been previously discussed elsewhere, but the primary objective of the authors is to review background knowledge and to draw attention to the practical applications of this material to toxicological problems. The succeeding chapters include infra-red analysis of expired breath after exposure to toxic gases and volatile liquids; analysis of basic drugs in biological specimens by ultraviolet spectrometry, gas-liquid chromatography, and ion-exchange paper chromatography; ionophoresis; sample preparation; and thin-layer chromatography in toxicological analysis. These chapters are valuable and interesting accounts of these techniques, and are full of useful tabulated data on compounds of toxicological significance. This book should be of interest and value to workers in many fields in which these techniques are of use. *R. T. Williams*

PARASITOLOGY

An Introduction to Parasitology, *by John M. Watson. Pp. vii+184. William Heinemann Medical Books, London. 1965. 20s.*

This book is one of a series of pharmaceutical monographs. The aim is to provide an up to date series of short publications for undergraduate students of pharmacy, and this book on medical and veterinary parasitology is admirably suited to this purpose.

There is an introduction in which parasites are briefly discussed in general terms. This is followed by chapters on protozoology, helminthology, entomology, and malacology, and on diagnosis, treatment, and prevention.

Brief descriptions of the commonest parasites of medical and veterinary interest are given, together with clear diagrams of many of them. The scarcity of labels on some of the figures, however, demands a knowledge which some students may lack. The descriptions should enable the student to distinguish most of the commoner parasites, but for many species he will have to refer to the larger textbooks of parasitology referred to in the bibliography. The descriptions are followed by accounts of the life cycle, the effects of the parasite on the host, and the treatment and prevention of the disease. All of this is concisely and lucidly written, and the accounts of treatment are especially valuable.

The book is well presented and can be recommended for students of pharmacology and also for all those who require an introduction to medical and veterinary parasitology. *D. L. Lee*

PHARMACOLOGY

Selective Toxicity, *by Adrien Albert. Third edition. Pp. xiii+394. Methuen & Co., London; John Wiley & Sons, New York. 1965. 63s.*

This is a fascinating book which gives a broad view of pharmacology. The earlier editions were also stimulating, but narrower than the present one. The improvement is very marked: the book is now well balanced.

Part I of the book, occupying one third of it, discusses general concepts and principles in pharmacology in an original and satisfyingly logical way. Some of the terminology is heterodox, but unusual terms are clearly defined and help towards understanding. Part II examines the relationship between chemical structure and biological activity. This part of the book is arranged along chemical lines, and includes chapters on metabolites and metabolite analogues, ionization, metal-binding substances, covalent bonds, steric factors, and surface chemistry.

The splendid thing about this book is the wealth of diverse and interesting examples given in every chapter, and the ample bibliography. However, a few of the medical uses of drugs mentioned have been superseded. The book is an excellent approach to pharmacology for anyone with an interest in chemistry who wants to transcend narrow medical or veterinary horizons. But it is not just an introduction: most pharmacologists, whether teachers or research workers, can gain new insights from it. *A. Herxheimer*

HISTORY OF SCIENCE

A Short History of Biology, *by Isaac Asimov. Pp. 180. Thomas Nelson & Sons, Edinburgh. 1965. 21s.*

To compress a history of 2000 years into less than 200 pages is a formidable task, demanding from the author a very high ability to select and evaluate. Dr Asimov's talents, although considerable, do not meet this exacting requirement. He gives us useful summaries of various aspects of biological history, but no uniformly authoritative account of the development of our understanding of living things.

The book is much stronger on medical topics than on others. Morphology receives almost no attention, and Goethe is not mentioned, despite his profound and curiously lingering effect upon biological thinking. Plants as a whole fare rather badly. The excitement that surrounded the first experimental investigations of photosynthesis, for example, deserves more than three lines.

There are other occasions when the reader begins to distrust Dr Asimov's judgment. His reference to Nägeli may serve as an example. Nägeli failed to realize the significance of Mendel's ratios, but he was nevertheless a first-rate scientist, and the first to infer the molecular structure of living matter from its physical properties. This pioneering work is ignored. *P. Bell*

The Background to Newton's *Principia, by John Herivel. Pp. xv.+337. Clarendon Press, Oxford: Oxford University Press, London. 1966. 70s.*

In this long-awaited study, Dr Herivel has executed his task with scholarly care and patience. As a result of a penetrating examination of Newton's early dynamical papers, he has greatly illuminated the technical and conceptual background essential for a deep historical understanding of the *Principia*.

The book is divided into two major sections. Part I, consisting of six chapters, discusses the main aspects of Newton's dynamical thought up to the period just prior to the publication of the *Principia* in 1687. The second part contains the manuscripts that are analysed, which are carefully transcribed.

At all times Herivel displays a full grasp of his material. Although intended for the specialist, the book contains a minimum of technical vocabulary and deserves to reach a wider audience. Herivel has made an important contribution to Newtonian scholarship, and the book will almost certainly become a classic in the field. *J. E. McGuire*

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Some books received

(*Note.* Mention of a book on this page does not preclude subsequent review.)

GENERAL SCIENCE

Chemistry and Biology Laboratories: Design, Construction, Equipment, *by Werner Schram (translated from the German by M. Jansen). Pp. x+255. Pergamon Press, Oxford. 1965. 105s.*

Man and Africa, *A Ciba Foundation Symposium, edited by G. Wolstenholme and M. O'Connor. Pp. xx+400. J. & A. Churchill, London. 1965. Cloth, 36s.; paper, 25s.*

La science contemporaine, *Vols. I and II, edited by L. Leprince-Ringuet. Librairie Larousse, Paris. Pp. 360, 1964, £7; pp. 360, 1965, £7.*

Women and the Scientific Professions, *edited by J. A. Mattfeld and C. G. Van Aken. Pp. xvii+250. The M.I.T. Press, Massachusetts and London. 1965. 53s.*

MATHEMATICS

Discourse on Fourier Series, *by C. Lanczos. Pp. viii+255. Oliver and Boyd, Edinburgh and London. 1966. 63s.*

The Mathematical Works of Isaac Newton, *Vol. I, introduced by D. T. Whiteside. Pp. xxi+160. Johnson Reprint Corporation, New York and London. 1964. 104s.*

The Mathematics of Matrices: A First Book of Matrix Theory and Linear Algebra, *by P. J. Davis. Pp. xiii+348. Blaisdell Publishing Co., New York, Toronto and London. 1965. 60s.*

PHYSICS

The Determination of the Time Position of Pulses in the Presence of Noise *by B. N. Mityashev (translated from the Russian by Scripta Technica Inc., edited by D. L. Jones). Pp. xv+190. Macdonald & Co., London. 1965. 80s.*

Electricity and Magnetism, *2nd edition, by B. I. Bleaney and B. Bleaney. Pp. xvi+764. Clarendon Press, Oxford; Oxford University Press, London. 1965. 70s.*

Encyclopedia of Physics, *Vol. III/3,* The Non-Linear Field Theories of Mechanics, *edited by S. Flügge. Pp. viii+602. Springer-Verlag. Berlin, Heidelberg, and New York. 1965. DM 198.*

Vth Inter-American Symposium on the Peaceful Application of Nuclear Energy, *held at Valparaiso, Chile, March 1964. Pp. vii+296. Pan American Union, Washington, D.C. 1965. $3.50.*

Low Temperature Behaviour of Solids: *An Introduction, by R. G. Scurlock. Pp. xvii+125. Routledge and Kegan Paul, London; Dover Publications, New York. 1966. 7s. 6d.*

Physics of High Pressures and the Condensed Phase, *edited by A. Van Itterbeek. Pp. xv+598. North-Holland Publishing Co., Amsterdam. 1965. 140s.*

Physics of Non-Crystalline Solids, *Proc. Int. Conf., Delft, Holland, July 1964, edited by J. A. Prins. Pp. xvi+667. North-Holland Publishing Co., Amsterdam. 1965. 180s.*

Radiation Damage in Crystals, *by L. T. Chadderton. Pp. xiv+202. Methuen & Co., London; John Wiley & Sons, New York. 1965. 36s.*

Some Electrical and Optical Aspects of Molecular Behaviour, *by M. Davies. Pp. x+190. Pergamon Press, Oxford. 1965. 15s.*

Theory and Practice of the Evaluation of Measurements, *by L. Jánossy. Pp. xxi+481. Clarendon Press, Oxford; Oxford University Press, London. 1965. 100s.*

CHEMISTRY

Advances in Physical Organic Chemistry, *Vol. III, edited by V. Gold. Pp. viii+282. Academic Press, London and New York. 1965. 63s.*

The Determination of Toxic Substances in Air, a Manual of ICI Practice, *edited by N. W. Hanson, D. A. Reilly, and H. E. Stagg. Pp. xii+200. W. Heffer & Sons, Cambridge. 1965. 50s.*

Crystal Structures of Minerals, *by L. Bragg, G. F. Claringbull, and W. H. Taylor. Pp. ix+409. G. Bell & Sons, London. 1965. 70s.*

High Pressure Chemistry, *by R. S. Bradley and D. C. Munro. Pp. vii+186. Pergamon Press, Oxford. 1965. 21s.*

Introduction to Stereochemistry, *by K. Mislow. Pp. xii+193. W. A. Benjamin, New York and Amsterdam. 1965. Cloth, $9.35; paper, $4.35.*

Investigations in the Field of Organolead Chemistry, *by L. C. Willemsens and G. J. M. van der Kerk. Pp. 133. International Lead Zinc Research Organization, New York. 1965. Free, from Lead Development Association, London.*

A Manual of Applied Chemistry for Engineers, *by F. G. Buttler and G. R. Cowie. Pp. xi+238. Oliver and Boyd, Edinburgh and London. 1965. 25s.*

Physical Principles of Chemistry, *by R. H. Cole and J. S. Coles. Pp. x+795. W. H. Freeman & Co., San Francisco and London. 1965. 68s.*

Trattato di Chimica Generale ed Inorganica, *3rd edition, by A. Ferrari. Pp. xxviii+1034. Casa Editrice Prof. Riccardo Pàtron, Bologna. 1965. 8500 lire.*

University Chemistry, *by B. H. Maham. Pp. xii+660. Addison-Wesley Publishing Co., Reading, Mass. 1965. 53s.*

BIOLOGY

Adaptation et agressivité, *edited by R. Kourilsky, A. Soulairac, and P. Grapin. Pp. xii+218. Presses Universitaires de France, Paris. 1965. 12 F.*

Bioenergetics, the Molecular Basis of Biological Energy Transformations, *by A. L. Lehninger. Pp. xv+258. W. A. Benjamin, New York and Amsterdam. 1965. Cloth, $6.60; paper, $3.25.*

Chromosomes, Giant Molecules, and Evolution, *by B. Wallace. Pp. xi+171. W. W. Norton & Co., New York. 1966. Cloth, $5; paper, $1.95.*

Les cultures organotypiques, *edited by J. André Thomas. Pp. vii+385. Masson et Cie, Paris. 1965. 90 F.*

Embryology of the Ovary and Testis, *Homo sapiens* and *Macaca mulatta, by G. van Wagenen and M. E. Simpson. Pp. 255. Yale University Press, New Haven and London. 1965. 56s.*

An Introduction to the Study of Tropical Plankton, *by J. H. Wickstead. Pp. 160. Hutchinson & Co., London. 1965. 25s.*

Manuel de biologie générale à l'usage des travaux pratiques, *Vol. I.* La cellule, *by R. Husson and F. Graf. Pp. 112. Gauthier-Villars, Paris. 1965. 22 F.*

BIOCHEMISTRY

The Biosynthesis of Macromolecules, *by V. M. Ingram. Pp. xv+223. W. A. Benjamin, New York and Amsterdam. 1965. Cloth, $8.80; paper, $4.35.*

Chemical Aspects of Polypeptide Chain Structures and the Cyclol Theory, *by D. Wrinch. Pp. 195. Munksgaard, Copenhagen. 1965. 35 Dan. kr.*

Histones and Other Nuclear Proteins, *by Harris Busch. Pp. xiii+266. Academic Press, New York and London. 1965. 76s.*

Mechanisms of Hormone Action, *edited by P. Karlson. Pp. 275. Academic Press, New York and London; Georg Thieme Verlag, Stuttgart. 1965. 116s.*

Organization for Protein Biosynthesis, *by A. Wiseman. Pp. ix+217. Blackwell Scientific Publications, Oxford. 1965. 45s.*

BOTANY

The Morphology of Gymnosperms, *by K. R. Sporne. Pp. 216. Hutchinson University Library, London. 1965. 15s.*

Organization and Evolution in Plants, *by C. W. Wardlaw. Pp xiii+499. Longmans, Green & Co., London. 1965. 60s.*

Plant Physiology, *Vol. IVA,* Metabolism: Organic Nutrition and Nitrogen Metabolism, *edited by F. C. Steward. Pp. xix+731. Academic Press, New York and London. 1965. $24.*

Ultrastructural Plant Cytology, with an Introduction to Molecular Biology, *by A. Frey-Wyssling and K. Mühlethaler. Pp. x+377. Elsevier Publishing Co., Amsterdam, London, and New York. 1965. 130s.*

ZOOLOGY

Fair Isle and its Birds, *by K. Williamson and P. Davis. Pp. xvi+311. Oliver and Boyd, Edinburgh and London. 1965. 30s.*

Laboratory Exercises in Zoology, *by E. Lendell Cockrum, W. J. McCauley, and R. Davis. Pp. xiv+388. W. B. Saunders Co., Philadelphia and London. 1965. 31s. 6d.*

The Life of Fishes, *by N. B. Marshall. Pp. 402. Weidenfeld and Nicholson, London. 1965. 63s.*

Regeneration in Animals and Related Problems, *edited by V. Kiortsis and H. A. L. Trampusch. Pp. xxiv+568. North-Holland Publishing Co., Amsterdam. 1965. 120s.*

MEDICINE

Antimicrobial Agents and Chemotherapy, *Proc. 4th Interscience Conf., New York, October 1964, edited by J. C. Sylvester. Pp. xiii+789. American Society for Microbiology, Michigan. 1965. $15.*

Isoantigens and Cell Interactions, *edited by J. Palm. Pp. 106. The Wistar Institute Press, Philadelphia. 1965. $5.*

Methodological Approaches to the Study of Leukemias, *edited by V. Defendi. Pp. 225. The Wistar Institute Press, Philadelphia. 1965. $7.50.*

Progress in Drug Research, *Vol. VIII, edited by E. Jucker. Pp. 530. Birkhäuser Verlag, Basle and Stuttgart. 1965. SFr. 115.*

Screening Methods in Pharmacology, *by R. Turner. Pp. xv+332. Academic Press, New York and London. 1965. 86s.*

AGRICULTURE

Essays on Crop Plant Evolution, *edited by Sir Joseph Hutchinson. Pp. vii+204. Cambridge University Press, London. 1965. 50s.*

ENGINEERING

Machine-Tool Vibration, *by S. A. Tobias (translated from the German by A. H. Burton). Pp. xvi+351. Blackie & Son, London and Glasgow. 1965. 65s.*

Plastics in Building Construction, *edited by R. M. Davies. Pp. ix+160. Blackie & Son, London and Glasgow. 1965. 45s.*

HISTORY OF SCIENCE

The Collected Papers of Lord Rutherford of Nelson, *Vol. III, published under the scientific direction of Sir James Chadwick. Pp. 428. George Allen and Unwin, London. 1965. 90s.*

A History of Parasitology, *by W. D. Foster. Pp. vii+202. 35s.;* A History of Immunization, *by H. J. Parish. Pp. xi+356. 50s. E. & S. Livingstone, Edinburgh and London. 1965.*

A Hundred Years of Chemistry, *3rd edition, by Alexander Findlay, revised by T. I. Williams. Gerald Duckworth & Co., London. 1965. 35s.*

Joseph Priestley, *by F. W. Gibbs. Pp. xii+258. Thomas Nelson & Sons, Edinburgh. 1965. 42s.*

Newtonian Studies, *by A. Koyré. Pp. viii+288. Chapman and Hall, London. 1965. 50s.*

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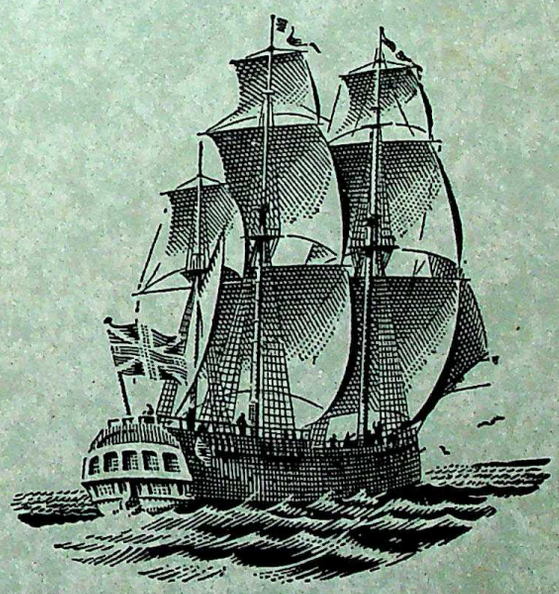

ENDEAVOUR

VOLUME XXV NUMBER 96 SEPTEMBER 1966

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Endeavour

Endeavour has been published by Imperial Chemical Industries since 1942. It presents, for scientists throughout the world, a regular review of the progress of science. While the emphasis is on British science, contributions are regularly commissioned from all parts of the world; the principal considerations are the intrinsic interest and importance of the subject and the authority of the writer. To ensure international acceptance, the journal is published in English, French, German, Italian, and Spanish.

No charge is made for *Endeavour*, and it is distributed to senior scientists, scientific institutions, and libraries throughout the world. Within these limits, the Editor is always glad to consider the addition of names to the mailing list.

The drawing on the cover is of the bark *Endeavour*, which, commanded by Captain James Cook and carrying a number of scientific workers, was sent out by the British Admiralty in August 1768, following a Memorial by the Royal Society to King George III, to chart the South Pacific Ocean and observe the transit of Venus.

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ENDEAVOUR

VOLUME XXV SEPTEMBER 1966

A review of the progress of science, published in five languages

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Communications should be addressed to the Editor, Endeavour, South Block, Thames House, Millbank, London S.W.1 Telephone: Tate Gallery 2181

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The Nobel Foundation

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The creation of the Nobel Foundation, set up at the beginning of the century to give effect to the wishes expressed by Alfred Nobel in his will, was fraught with considerable legal difficulties. Once these were resolved, however, the complex arrangements made for choosing the prize-winners worked well, and over the years the award of Nobel Prizes has been accepted as the highest form of international recognition in the several fields in which they are given. The impartiality of the judges, and the great care they take in reaching their decisions, are generally recognized. Nevertheless, seventy years have now elapsed since Nobel's death in 1896, and during those years great changes have occurred in the scientific world. The enormous enlargement of the scope of science, and the manifold increase in the number of research workers involved in extending its frontiers, mean that in many contexts methods found perfectly satisfactory at the beginning of the century need to be looked at anew. It is against this background that the Nobel Foundation has carried out a reappraisal of some of its objects and the best means of attaining them. It has now announced changes that are of interest to all scientists.

The Foundation's statutes were formally promulgated on June 29th 1900. They govern not only its own activities but those of a number of important bodies concerned with selecting the prize-winners. Firstly, there are four prize-awarding bodies: namely the Royal Academy of Science (for physics and chemistry); the Royal Caroline Medico-Chirurgical Institute (physiology or medicine); the Swedish Academy (literature); and the Norwegian Storting (peace). Five Nobel Committees (one for each prize-group) revise the list of proposed candidates and make recommendations to the prize-awarding bodies. The Committees have three to five members each; they may consult with experts in any part of the world to assist them in their task. Besides, there are four Nobel Institutes, originally set up mainly to assist the prize-awarding bodies in carrying out investigations necessary to making their recommendations. Over the years, however, those for physics, chemistry, and medicine have developed into valuable research institutions, and those for literature and peace have set up important libraries.

In order that no potential candidate shall be overlooked, nominations are invited from many different sources in many different countries. These include former Laureates, certain designated professors, and the prize-awarding bodies. Every nomination is essentially an individual one; even in the case of the prize-awarding bodies it is their members, and not the bodies as such, who have the power of nomination. Nominations must be received by January 31st each year; then follows long committee work in secret, culminating in the announcement of the awards in October or November and their presentation in Stockholm and Oslo on December 10th, the anniversary of Nobel's death.

The Foundation's plans involve organizational changes which put larger funds at the disposal of the prize-awarding bodies. Three of the Institutes have been disposed of. That for physics and for chemistry has been sold to the Swedish Government, becoming a State Institute for Nuclear Research. The Nobel Institute for Medicine remains in the possession of the Foundation, but its operation is now financed by the Government. In addition, the Foundation has lately received from the Bank of Sweden Jubilee Fund a substantial grant to promote international activities.

In formulating their new plans, the prize-awarding institutions—especially in the science fields—have recognized that one of the great needs is an improvement in the effectiveness of exchanging scientific and other information. While entirely new methods—particularly those based on computers—are being introduced to alleviate an almost unmanageable situation, there are still long delays between new discoveries being made and knowledge of them reaching research workers.

The Foundation, recognizing that the problem as a whole has become too big for even its considerable resources, has resolved on a specialized approach which is both in keeping with its ideals and makes use of its unique international network of scientific contacts. It will organize international symposia, each attended by only a very limited number of specially invited participants; the smallness of the groups, and the fact that every member will be a leading expert, will encourage very full and frank exchanges of views. Although the symposia themselves will be limited to a scientific élite, provision will be made for summaries of the discussions and conclusions to be made public. The first symposium of this kind—on neurophysiology—was held under the direction of Professor Ragnar Granit of Stockholm.

The proper administration of the Nobel Funds puts a great responsibility on all concerned, and demands a thorough knowledge of recent developments. The symposia will assist with this, but other moves have been made to enable members of the prize-awarding bodies to keep themselves up to date. These include improved documentation and translation services; greater utilization of Swedish and foreign experts; and the inviting to Sweden of guest lecturers and research workers. Relieved of the responsibility for research at its Nobel Institute, the Royal Academy of Sciences is free to devote considerable effort to developing these new activities.

The proposals outlined above relate mainly, of course, to the prizes for science and medicine, but under the terms of the will those for literature and peace are of equal importance, and for them also there are new plans to help the adjudicators. These include lectures by prominent cultural and literary representatives, and steps to assess literary attainments in the world's less familiar languages.

Apart from their importance in maintaining, in the circumstances of today, the Nobel Foundation's reputation for the impartial recognition of merit wherever it may be found, these proposals have a much wider significance. The Foundation, with its great resources, has found new ways of making a direct contribution to the progress of science and establishing contact with the international scientific community generally. For these reasons, as much as for their value in enabling the Foundation effectively to discharge its obligations in awarding the prizes, the new proposals will be generally welcome. A not unimportant consideration is that the modern world tends to view with some reserve wealthy corporations which seem to stand aloof from current affairs. In embarking on these new activities, the Foundation surely serves its own best interest as well as that of science generally.

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Viral carcinogenesis

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Michael Stoker

Although no true cancers of man have yet been shown to be caused by viruses, there are a number of viruses that can chronically infect man and can cause tumours in other animals under laboratory conditions. This article discusses the mechanism of the transformation, by a virus containing DNA, of a normal cell into one that will grow into a tumour. It also considers the relevance of this mechanism to an understanding of the processes that cause naturally occurring cancers. These may involve the action of fragments of genetic material similar to viruses.

Human beings, and probably all animals, commonly harbour viruses as long-standing latent infections, sometimes lasting for life; it is now apparent that many of these commensal viruses are capable of causing cancer of similar tumours. A few viruses that will cause tumours have been known since the early work of pioneers such as P. Rous, R. E. Shope, and J. J. Bittner, but they were for a long time considered to be rarities of no general interest, and work on them was overshadowed by research on chemical carcinogens. However, L. Gross found, in the 1950s, that leukaemia in mice could be transmitted by the inoculation of newborn animals; this led to a more general use of this technique, and thence to the recent discovery of a variety of new carcinogenic viruses.

Concurrently with the discovery of these viruses, new approaches have been made to understanding the basic mechanisms involved in viral carcinogenesis. These approaches were largely initiated by H. Rubin with one of the classical tumour viruses, the Rous sarcoma virus of chickens, but have since been extended to many of the newer agents. New techniques, particularly the carcinogenic transformation of isolated cells in culture under controlled conditions, have made it possible to use the more precise methodology and approach developed in research on bacterial viruses.

All this has led, in the last decade, to a large increase in research on tumour viruses in all aspects, including extensive studies of the possibility that viruses cause cancer in human beings.

Oncogenic viruses

At least 40 viruses have now been isolated which are oncogenic, that is, capable of inducing tumours in mammals, birds, or amphibia. Some of these viruses are closely inter-related, but they fall into at least six distinct groups on the basis of structure and behaviour. From this, it is clear that tumour viruses are not all alike, and they include representatives of the two main classes of viruses. In one of these, the genetic material is deoxyribonucleic acid (DNA); in the other, ribonucleic acid (RNA). The 'DNA tumour viruses' at least are known to vary greatly in their size and therefore in the amount of genetic information carried.

It was previously believed that the action of each of the tumour viruses was limited to one particular host, but many of these viruses have now been found capable of causing cancer in more than one species. Certain variants of the Rous sarcoma virus that have been isolated are of particular interest, because they can act on mammals as well as birds. The investigations of H. Hanafusa, P. Vogt, and others have now shown that the nature of the host attacked by this virus depends, not on the Rous virus itself, but on an associated or 'helper' virus. The helper virus is necessary because the Rous virus is defective and cannot direct synthesis of its own virus coat—the layer around the nucleic acid. Various helper viruses can provide alternative coats for the Rous virus, and the particular virus coat determines which host the Rous virus can infect. Recently, a helper virus that enables the Rous virus to infect and cause tumours in mammals has been identified.

Each tumour virus is not limited to a single form of cancer, because the same virus can initiate the change in differentiated cells of more than one type and in different situations, thus leading to a variety of different forms of the disease. Evidence has also been produced recently by P. Black that a single cancer cell can differentiate in more than one way, thus giving mixed tumours with more than one type of cell.

As found in nature, tumour viruses may be considered in two groups relating to cancer in their normal hosts. One group is oncogenic under natural conditions; the other is not.

Many viruses have been isolated from naturally occurring tumours and from healthy animals prone to such tumours, and these viruses have been found capable of reproducing a similar disease after transmission under natural or experimental conditions. These viruses include the two major groups of viruses responsible for a variety of forms of leukaemia in chickens and mice respectively, and the virus of mouse mammary cancer. Another large group of naturally occurring tumours induced by viruses are the papillomas, or warts, well known in humans, but also common in rabbits, dogs, cattle, and probably many other animals. To a pathologist, papillomas are not cancers because they do not spread, but the initial action of the papilloma viruses is probably similar to that of close relatives that cause true cancers.

Members of another class of viruses produce cancer very readily when inoculated into experimental animals, but cannot yet be related to naturally occurring tumours in any animal. These viruses include polyoma virus of mice, SV40 virus of monkeys, and adenoviruses from man, monkeys, and cattle. These viruses are of particular interest because they are very common, and are found as persistent latent infections in a high proportion of their

M. G. P. Stoker, *M.D., F.R.S.E.*
Was born in 1918 and educated at the Universities of Cambridge and London. He served in the Royal Army Medical Corps in India during the second world war, and he conducted research at the University of Cambridge from 1947 to 1958. He is now the Professor of Virology at the University of Glasgow and the Honorary Director of the Medical Research Council Experimental Virus Research Unit, Glasgow.

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normal hosts. We shall consider later why tumours caused by these viruses do not occur, or have not been detected, under natural conditions.

Carcinogenesis by viruses containing DNA

As already mentioned, there are two distinct groups of tumour viruses, containing DNA and RNA respectively. On theoretical grounds these would be expected to differ in their mode of action, and this supposition is supported by the available evidence. The following account will be restricted to the studies on some DNA-containing viruses —adenovirus, polyoma virus, and SV40 virus: it will be particularly concerned with the last two, whose mode of action has been intensively investigated in cultured cells.

When cultures of living fibroblastic cells are exposed to either polyoma or SV40 virus there are two possible manifestations of infection. The virus may grow vegetatively, destroying the cells and releasing large numbers of newly synthesized virus particles. Alternatively, the cells may survive and some of them may show new hereditary characteristics typical of cancer cells. This second effect of the viruses is known as neoplastic transformation or viral transformation.

Vegetative growth

The vegetative growth of polyoma and SV40 viruses superficially resembles vegetative growth of other viruses not known to be oncogenic, and using suitable cells where this type of growth predominates, the virus particles can be counted because of their ability to produce foci of cell degeneration, or plaques.

The growth cycle in individual cells lasts about 24 hours and ends with release of the virus, and death of the cell. During at least the early part of this period, however, the normal cellular synthetic processes continue, and under certain circumstances polyoma virus will even stimulate the synthesis of cellular DNA that precedes the synthesis of new copies of viral DNA. This is in contrast to the inhibition of synthetic processes that is commonly caused by some viruses which are not oncogenic. During vegetative growth, the viral DNA directs synthesis of several virus proteins, three of which may be detected by immunological techniques as antigens. Two probably distinct antigens appear early and may be concerned with the initiation of the DNA replication process. One appears later and is known to be the constituent protein of the virus coat, which is finally assembled round the newly synthesized DNA molecules before the virus is released from the cell.

Neoplastic transformation

The other activity of the virus, leading to transformation of a normal cell into a tumour cell, may be recognized in cell cultures because transformed cells have altered growth characteristics. On the solid glass surface of a culture vessel, they give rise to round colonies of randomly arranged cells that can easily be distinguished from the sheaflike colonies of parallel normal fibroblasts.

A more accurate and sensitive method of detecting transformations has been developed from the observation that transformed cells, but not normal cells, will grow when suspended in fluid or a soft gel. If, therefore, cells are exposed to virus and cultured in soft agar, the transformed cells alone grow into colonies which can be seen

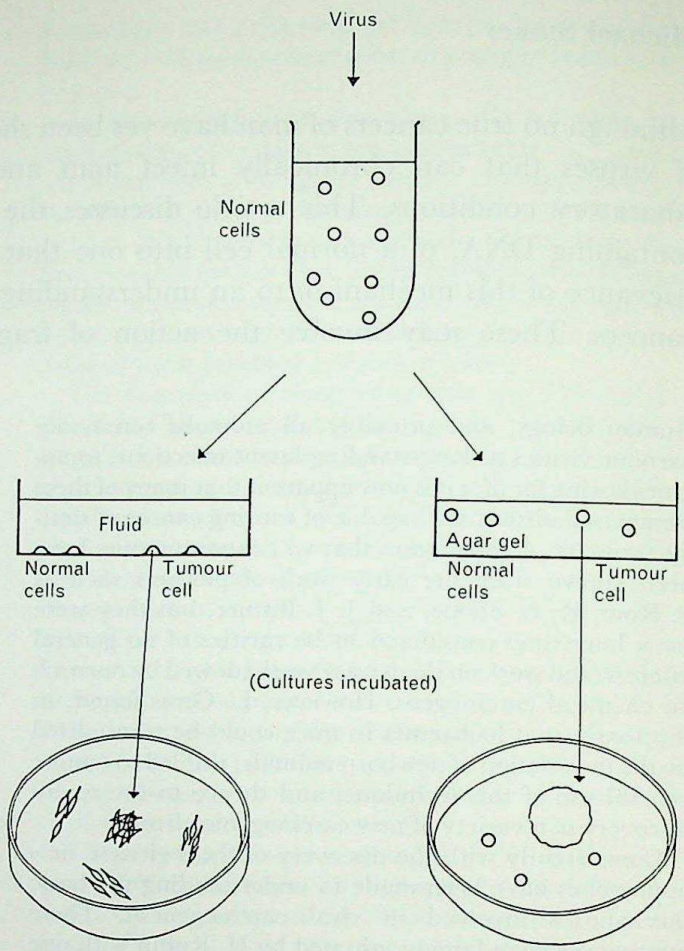

Figure 1 Two methods for detecting transformation of normal cells into tumour cells following infection with polyoma virus. On left: Both normal and tumour cells grow on glass surface, but colonies can be distinguished. On right: Only tumour cells grow in agar gel.

and counted even without the aid of a microscope. Both these methods, the first non-selective, the second selective, for detection and counting of transformations are in common use and are illustrated in figures 1 and 2.

It can be shown by such techniques that a single isolated cell can be transformed as a direct result of infection with a single particle of virus. This rules out the possibility of the emergence, by selection, of pre-existing tumour cells. It also excludes co-operation between cells, for example by carcinogenic products of an infected cell causing transformation of uninfected cells.

It can also be shown that transformation, as well as vegetative growth, can be brought about by isolated viral DNA. The DNA which can be extracted from virus particles is in the form of a double stranded ring, which is either open or twisted: less commonly it is found as a linear molecule caused by breakage of the ring. Figure 3 shows electron-micrographs of the ring forms, and, on the same scale, virus particles from which they are obtained. Studies using these different types of DNA to infect cells show that both vegetative growth and transformation can be initiated only by circular molecules, but it has not been possible to identify any unique type of molecule responsible for transformation alone.

Though the operative transforming unit is a molecule of DNA from a single virus particle, the probability of initiating transformation is very low, since on average nearly a million virus particles are needed for every

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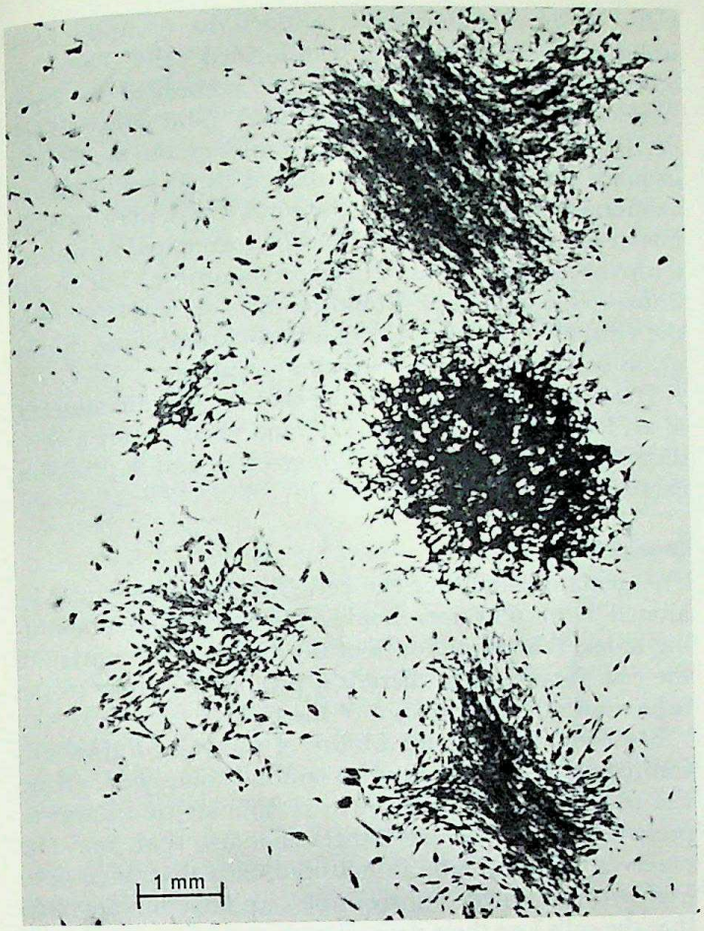
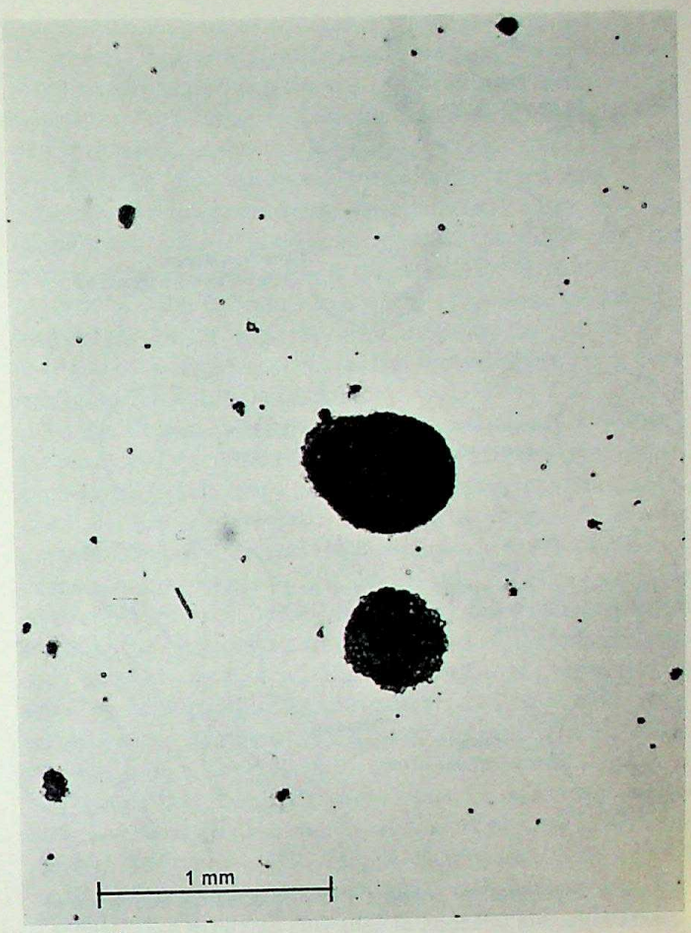


Figure 2(a)



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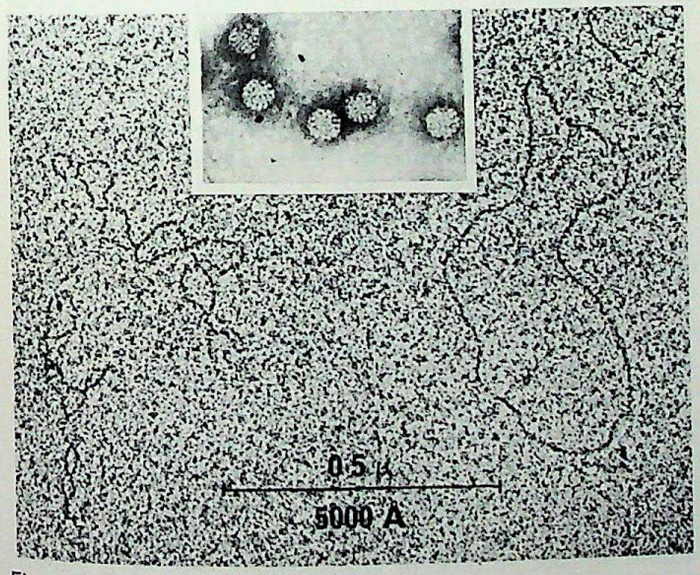

Figure 3

Figure 2 (a) Colonies of fibroblasts grown on solid surface after exposure to polyoma virus. Dense irregular colony in centre is derived from a transformed cell. Remaining colonies are from normal cells. (See figure 1, left.) (b) Colonies of fibroblasts grown in agar gel after exposure to polyoma virus. Two dense spherical colonies have arisen from transformed cells. Remaining normal cells have not grown. (See figure 1, right.)

Figure 3 Molecules of DNA from polyoma virus demonstrated by electron-microscopy using the Kleinschmidt technique. (This increases the apparent thickness but not the length of the strand.) Two supercoiled molecules on left, open molecule on right. Inset: Particles of polyoma virus at same magnification. (Preparations by Dr E. A. Follett, Institute of Virology, Glasgow.)

successful transformation, even under optimal conditions. This may be relevant in explaining why tumour viruses are commonly present in their natural hosts without giving rise to tumours.

Cells transformed by DNA viruses have two important characteristics. Firstly, they are permanently endowed with at least two new antigens. Since the specificity of these antigens depends on the original virus and is independent of cell type, it can be assumed that they are proteins specified by viral DNA present in the transformed cells.

Secondly, vegetative growth and the production of virus particles does not take place in the great majority of transformed cells. (This is in contrast to tumours induced by RNA viruses which do permit continuous synthesis of new virus.) The new antigens which appear in transformed cells appear to be the same as early antigens made in vegetative growth of the virus, but there is no synthesis of viral coat protein, no sign of mature virus particles, and of course, no destruction of the cells.

Since transformation is not accompanied by full vegetative growth and since vegetative growth is probably lethal, the two are mutually exclusive and it becomes clear why these are alternative results of infection.

Partial failure of viral activity in transformed cells

It has been shown that the viral proteins associated with the early stages in vegetative growth are also synthesized in transformed cells, but the component proteins of the mature virus particle, which appear later during vegetative growth, are neither made nor assembled. Thus the infection in transformed cells may be regarded as stopping

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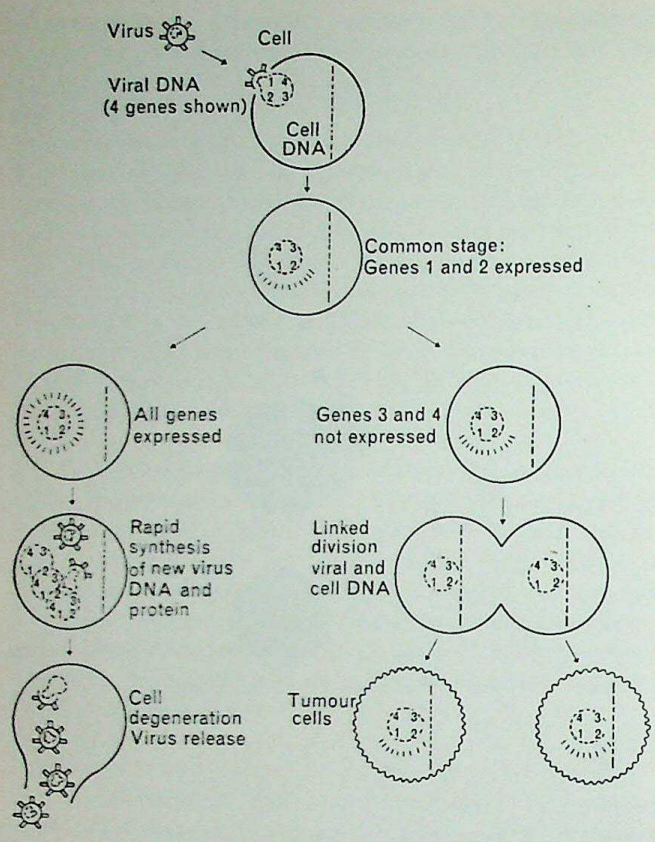

Figure 4 Hypothetical scheme showing possible sequence of events following infection of cells with small DNA-containing tumour viruses.

before some of the later processes that normally occur during vegetative growth and result in the death of the cell. The outcome of an infection in a particular cell may therefore depend on whether these late processes come into play at a critical stage in the infective process. This is illustrated in figure 4, which is a hypothetical representation of the alternative possible events following an early stage of infection.

The size of a polyoma DNA molecule suggests that the information is carried by between 4 and 8 genes. An unknown number of these code for proteins concerned in the initial events, common to transformation and vegetative growth, and others code for proteins required later, for example, the virus coat and its assembly. We can only guess at the various possible ways in which the genes responsible for these later processes might fail operationally. For example, the part of the DNA containing these genes may be missing or altered in occasional mutant particles of virus, or transcription may be suppressed, as occurs in lysogenic bacteria. Alternatively the viral DNA may operate normally but certain cells may misinterpret the code in one of the late-acting genes and give rise to the wrong protein, or to no protein at all. These and other possible mechanisms may be surmised from the more advanced work on bacterial viruses.

Transmission to cell progeny

Though there is no evidence for synthesis of mature virus, the early functions, as represented by the new antigens, continue in all the descendants of the initially transformed cell. This implies the continued presence of viral DNA, and also its multiplication in step with cell division. This DNA must be very efficiently distributed to daughter cells, because cells without antigen have rarely been isolated in the progeny of transformed cells. The high efficiency of transmission could be accounted for by a large number of copies distributed randomly at cell division, but the large amount required on theoretical grounds has not been demonstrated by direct chemical examination. Alternatively the viral DNA may exist as one or a few copies per cell, and be segregated at mitosis with the chromosomes. The most plausible, but as yet unproved, explanation would be physical attachment of the viral DNA to the DNA of a host chromosome (figure 4), as occurs in bacteria carrying prophage.

It is, as a contrast, interesting that the genetic material of an RNA virus, the Rous sarcoma virus, is not always distributed efficiently to daughter cells, and is probably carried in a different way.

Change in phenotype

The genetic content of the cell (the genotype) may be altered by the addition of only a few viral genes, amounting to less than a millionth of the genetic information of the cell. Nevertheless there is a profound change in the behaviour (the phenotype) of the cell.

Most important is the ability of the cell to grow unrestrictedly in the tissues of the animal concerned, giving rise to a tumour. This growth is difficult to analyse at present, but there are other changes that may be observed more directly in cultured cells that have been freshly transformed. For example, we have already seen that the cells lose their dependence on anchorage to solid surfaces and can grow in fluids or soft gels. They also acquire the ability to move freely and to multiply even when crowded into close contact with one another, when normal cells are subject to an important regulation process known as contact inhibition. All these features may be of considerable relevance to the behaviour of the cancer cells in the animal.

The relationship of the persistent viral genes to the new cell phenotype remains a central problem. One of the two known viral antigens is of a type known in normal cells as a transplantation antigen. This is thought to be present on the cell surface and as its name suggests, is involved in the recognition of differences between individuals of the same species. The simple hypothesis would be that the cell surface is altered by the acquisition of one or more proteins specified by the integrated viral DNA, and that all the phenotypic changes follow. So far, apart from the implied presence of new viral antigen, the only change found in the surface of transformed cells is a raised negative surface charge due to an increase in a mucopeptide, sialic acid.

This simple explanation of surface change is attractive but, even if true, the changes in the phenotype of the cell will not be understood until more is known of the way in which surface components affect the behaviour of normal cells.

Viruses and cancer in man

The majority of studies on virus and cancer, either at the level of cells or whole individuals, have been concerned with cancers of mammals other than man, and birds. What are the implications for cancer in man?

Firstly, it should be made clear that no true cancers of man have yet been proved to be caused by viruses or any other micro-organisms. Nevertheless the common

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wart, though not a cancer, is due to a virus that is closely related to many true cancer viruses of animals. Particles resembling viruses have been seen with the electron microscope in material from patients with leukaemia, though the only agent so far isolated and grown in the laboratory was eventually identified as a mycoplasma, which is a very small bacteria. A much more typical looking virus has been seen in cultured cells from Burkitt's tumour, a common cancer in African children that has been suspected from its geographical distribution to be due to a mosquito-borne agent. The general problem is to determine whether any virus that is found in the tumours originally initiated the primary cell transformation, perhaps many years previously, or whether it is merely a passenger virus which commonly contaminates the tumour tissue as a secondary invader.

No virus isolated from human tumours has been found to cause cancer in animals, and inoculation of human beings is obviously unacceptable. It is now possible, however, to test the activity of viruses in cultures of human cells. One virus, SV40 virus, from monkeys, has in fact been found to induce typical transformation of cells from human embryos and from human foreskins. This is not a virus which occurs naturally in humans but a large number of individuals have been infected in the past through unrecognized contamination of vaccines. The surveillance of these individuals over many years has not however revealed any unusual increase in the incidence of cancer.

Perhaps the most significant finding in recent years has been the discovery that in spite of this, several types of adenoviruses isolated from humans will induce experimental cancer in animals, and also in cultured animal cells. Adenoviruses are large, DNA-containing viruses that are well known as the cause of various mild illnesses affecting the nose, eyes, and respiratory tract. Several types, including those that are oncogenic, are also known to persist as latent infections in healthy individuals, in the same way as tumour viruses such as polyoma and SV40 viruses in animals.

Whether or not these potential carcinogens cause human cancer is at present unknown. As already stated, the experimental induction of tumours depends on inoculation of newborn animals, and the first infection of humans probably occurs most frequently after the critical sensitive period, so that natural adenovirus tumours might anyway be rare. Adenoviruses have not been isolated from human cancer but this might be expected; as has been mentioned, viruses are not produced in tumour cells. Antigens specific to adenovirus should perhaps be detectable, but so far none have been reported in human tumours.

In man, therefore, the situation seems to be similar to that found in many animals. They are persistently infected with viruses which are highly carcinogenic in the laboratory, but not, apparently in nature. This could be explained by supposing that cell transformations do occur from time to time *in vivo* under natural conditions, but that the new antigens acquired by the cells lead to rejection by the immunity mechanisms of the host. Tumours would not appear except where these mechanisms were undeveloped and where high doses of virus might cause a large enough number of cell transformations to survive the immunological response. This situation might follow experimental inoculation of newborn animals with high virus doses, but would occur only very rarely under natural conditions.

It is still possible however, that infections involving certain virus variants or types of cells might result in an even greater deficiency of the virus genetic material than that already discovered. If so, this might result in perpetuation of the viral DNA without the production of those virus proteins which cause an antigenic change leading to rejection of the cells. Such cells might still have some of the phenotypic manifestations of transformation and through lack of an immune response, they might grow successfully and form a cancer; moreover the usual viral specific antigens would not be detected in these cancers even if the causative virus were known.

Though this is highly speculative, it is important to bear in mind the extent to which viral material may remain hidden in a cell. This is clearly shown by recent work with certain defective bacterial viruses whose presence in the host cell can only be revealed by 'rescue' with other viruses. This operation depends on sophisticated genetic experiments, however, and it will be many years before such techniques can be usefully applied to animal viruses and cells. Nevertheless it might ultimately turn out that independent fragments of virus-like genetic material, perhaps assisted at certain stages in their existence by viruses proper, are the key to many naturally occurring tumours. If so, arguments about the viral aetiology of cancer will finally turn on the definition of the word 'virus'.

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Unarmoured marine dinoflagellates

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Richard E. Norris

The dinoflagellates are part of the marine plankton population, and are important for their share in the primary productivity of the sea. In addition, their evolutionary history places them in a phylum containing no other creatures. The armoured dinoflagellates, which secrete a hard coating, have been studied for some time, but the unarmoured dinoflagellates are so difficult to preserve that little is known of them. This article surveys what has been found out in a shipboard laboratory.

The phytoplankton—minute chlorophyll-containing organisms—represent a large part of the primary productivity of the sea, and the marine phytoplankton populations are often mainly composed of diatoms. Other types of organism, such as dinoflagellates and coccolithophorids, which are often very common in marine plankton, have recently become of interest. Coccolithophorids are minute flagellated photosynthetic cells belonging to the Chrysophyta and were recently discussed in ENDEAVOUR by M. Black [1]. This article will be concerned with one section of the dinoflagellates.

Dinoflagellates are placed in a phylum designated for them alone, the Pyrrophyta. Like diatoms and coccolithophorids, certain dinoflagellates produce a wall material, probably partly cellulose, that is preserved by the fixatives that are used in microscopy and that can be recognized in non-living plankton samples. These dinoflagellates are called the armoured forms, and they produce a series of plates that have distinctive shapes, sizes, and alignment for each of the various species (figures 1 and 2). There are other dinoflagellates that produce no plates of armour and are quite devoid of wall materials (figures 3–19). These naked (unarmoured) cells are usually unrecognizable in preserved plankton samples, because the cell membrane does not retain its shape in such commonly used preservatives as formaldehyde. As a result, the unarmoured dinoflagellates cannot be counted in plankton analyses of preserved samples. They are often so delicate that they perish when placed in light of high intensity or in temperatures higher than their natural environment; the cells therefore often burst while being examined with a microscope. Being so difficult to observe, and almost impossible to preserve, it is not easy to estimate the importance of unarmoured dinoflagellates in the total primary productivity of the sea.

Our knowledge of them began with the classic investigations of F. Stein, O. Bütschli, and G. Pouchet, and culminated with the monographs of C. A. Kofoid and O. Swezy [2], M. V. Lebour [3], and J. Schiller [4]. Recent research has added to the number of species known in the sea and has contributed to our knowledge of certain species in laboratory cultures [5]. Most of the species known today probably live entirely in coastal waters, as the truly oceanic types do not usually survive a transfer to land-based laboratories. However, because of the closeness of oceanic currents to the coast of southern California, Kofoid and Swezy [2] were successful in obtaining live specimens of what was probably an oceanic type, and were able to study them in the laboratory. Similar conditions at some seasons in the Mediterranean and off the coasts of Great Britain have encouraged studies in these regions. The vast oceanic regions, however, are almost completely unexplored for unarmoured dinoflagellates, which have to be investigated in shipboard laboratories, where they can be photographed. Some of the photographs of these phytoplankton cells, taken during the first two cruises of the United States *R/V Anton Bruun* in the International Indian Ocean Expedition, are used in the following discussion.

Richard E. Norris, *B.S., Ph.D.*

Was born in Seattle, Washington, in 1926, and educated at the University of Washington and the University of California at Berkeley. He was employed by the Radiation Laboratory, University of California, from 1953 to 1955 and was on the staff of the Botany Department of the University of Minnesota from 1955 to 1962. Since 1963 he has been on the staff of the University of Washington. His particular research interests are behaviour studies and cytology of marine phytoplankton and morphology and phylogeny of red algae.

The unarmoured dinoflagellate cell

Dinoflagellate cells are very complex, exhibiting a wide variety of structure and form and containing many different organelles, some of which are unique to this group of organisms. The cells of most dinoflagellates are orientated from top to bottom, and two flagella producing quite different movements are attached on the ventral (lower) side of the cell, and located within two distinct grooves (figure 9) of the cell surface membrane. In the girdle groove, which encircles the cell, lies a flattened ribbon-like flagellum that beats with a rapid helical action in the groove; this motion seems to cause most of the forward thrust of the cell. The cell swims rapidly in a spiral path, often rapidly rotating in either direction on its own body axis. T. L. Jahn, W. M. Harmon, and M. Landman [8] attribute part of the force from the girdle flagellum to its push against the inner flange of the groove. The second flagellum lies in a longitudinal groove, the sulcus, that extends toward the posterior on the ventral side of the cell. In some species a flange of the cell overlaps the sulcal groove, sometimes forming a complete covering to the channel (figure 15). The flagellum in this groove occasionally seems less active than the girdle flagellum and beats in a planar wave, probably contributing to the spiral path of the cell as well as to the forward propulsion. The force causing cell rotation was attributed to the shape of the cell in *Ceratium* (an armoured genus with long horns) [8], but remains unexplained in less unusual species. It seems possible that the angle of the groove may play a major role in the rotation of dinoflagellate cells.

Unarmoured dinoflagellate cells include a wide range of shapes, from almost spheres (figures 3, 4, 7, and 9) to long, attenuated cylinders and ellipses (figures 14 and 16). The ventral face is usually flattened or concave, the dorsal (upper) side is convex. It is interesting that the shape of many species suggests that they have become more streamlined during their evolution (figures 5, 6, 8, 14, and 16). A streamlined body of a size comparable to a dinoflagellate cell would have approximately 20 per cent less drag than a large spherical-shaped body with

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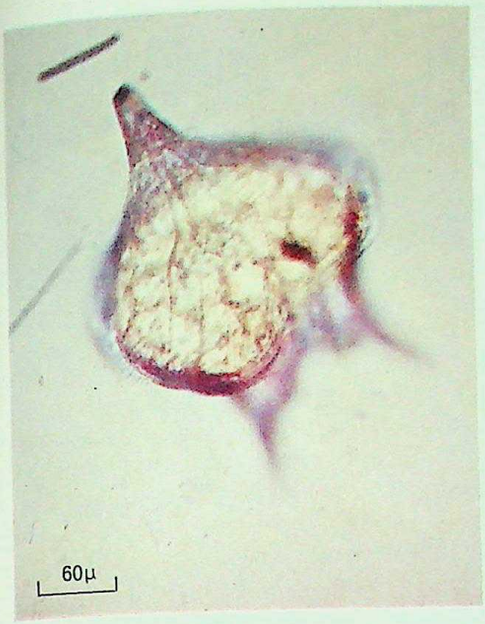

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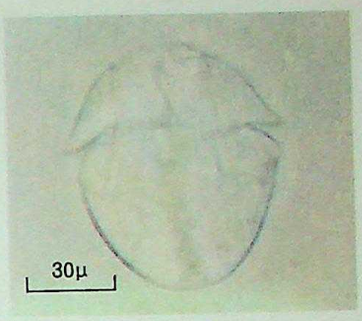

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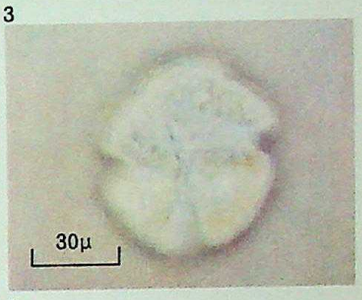

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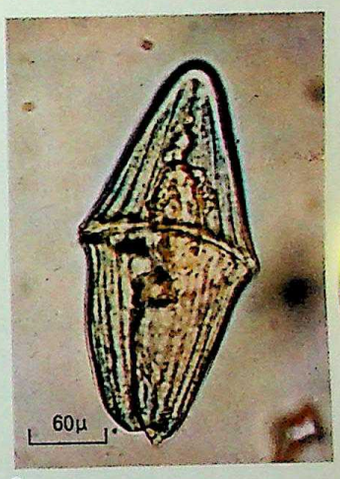

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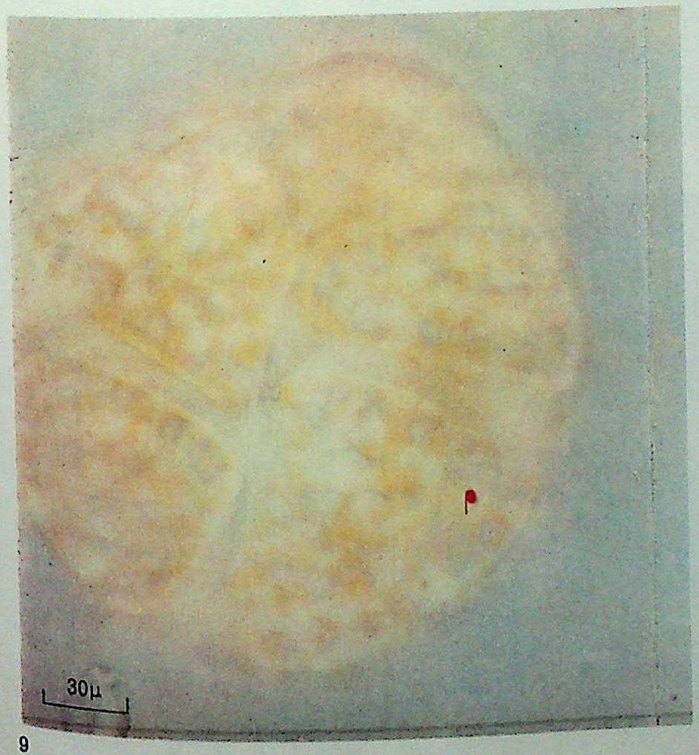

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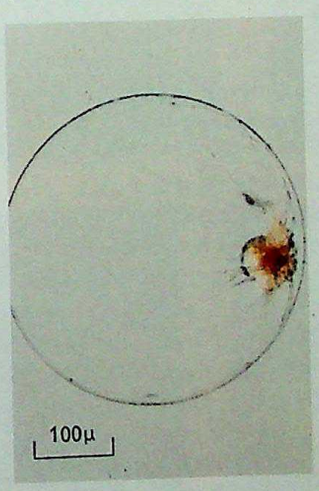

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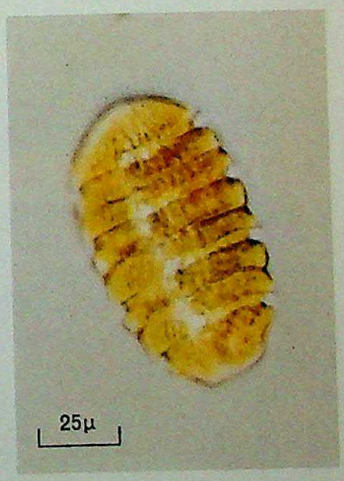

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Figure 1 *Peridinium* (possibly *P. remotum*).
Figure 2 *Peridinium diabolus.*

Figure 3 *Plectodinium* sp. (ventral view).
Figure 4 *Gyrodinium* sp. (ventral view).
Figure 5 *Gyrodinium* sp. (ventral view).
Figure 6 *Amphidinium* sp.
Figure 7 *Gymnodinium* sp.
Figure 8 *Gyrodinium* sp. (dorsal view).
Figure 9 *Gyrodinium* sp. (ventral view).
Figure 10 *Pyrocystis pseudonoctiluca.*
Figure 11 *Phaeopolykrikos beauchampii* (ventral view; in culture isolated from Friday Harbor, Wash.).

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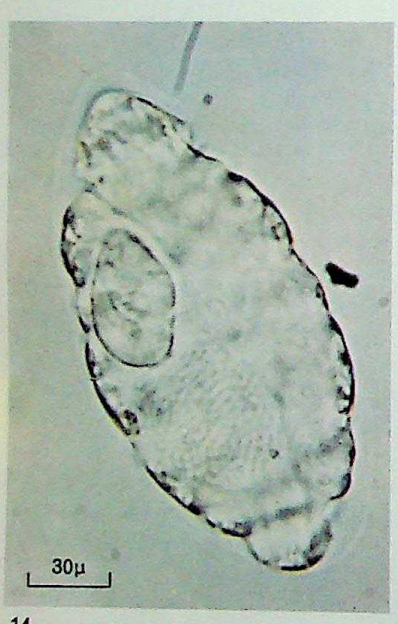

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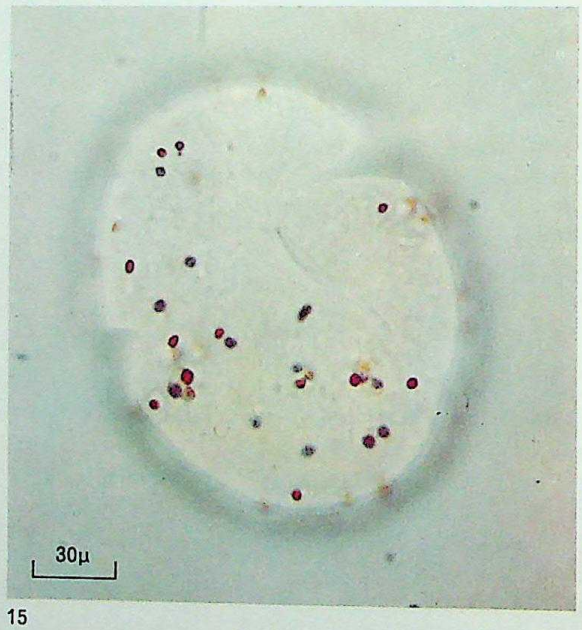

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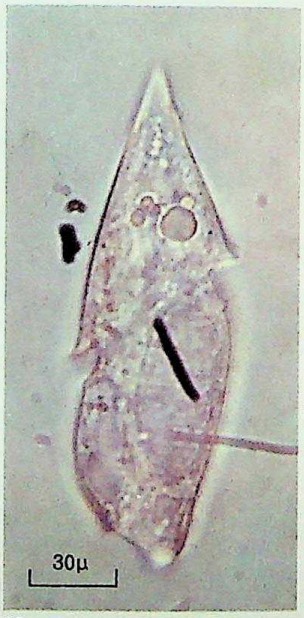

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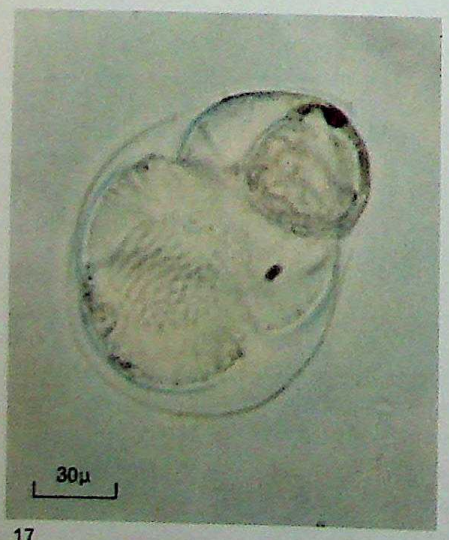

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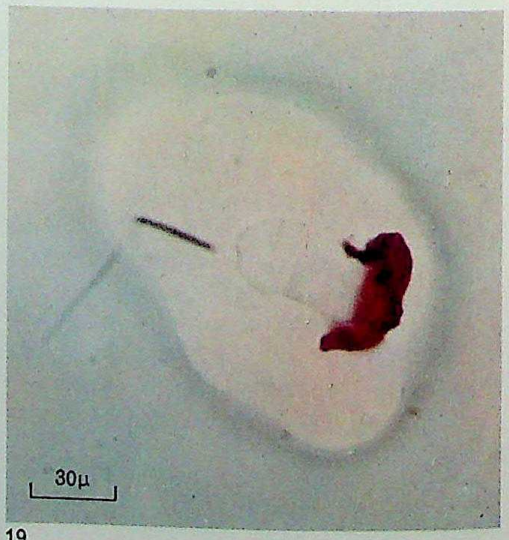

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Figure 12 *Cochlodinium* sp. (ventral view).
Figure 13 *Cochlodinium* sp. (optical section, showing nucleus).
Figure 14 *Cochlodinium* sp.
Figure 15 *Gymnodinium* sp. (ventral view).
Figure 16 *Gyrodinium* sp. (dorsal view).
Figure 17 *Warnowia* sp. (possibly an encysted cell, pigment body is very small).
Figure 18 *Warnowia* sp. (ocellus with a very large pigment body).
Figure 19 *Warnowia* sp. (ocellus with a laminated lens).

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the same surface area. This is a significant reduction in drag, and presumably confers an advantage in natural selection.

Dinoflagellate cells range in size from extremely minute forms, with a diameter of approximately 5 μ to very large species with cells visible to the naked eye (*Pyrocystis* (figure 10), *Noctiluca* (figure 25), *Polykrikos*, for example.) The very small species (figures 4 and 7) are usually highly motile, and do not sink as rapidly as the larger cells because of the increased effect of friction in relation to volume in smaller bodies. Large forms (figure 10) are often spherical and usually contain an enormous vacuolar system that probably contributes to cell buoyancy. The buoyancy mechanism of *Noctiluca* has already been described in ENDEAVOUR [15]. C. W. Beklemishev, M. N. Petrikova, and H. J. Semina demonstrated [10] that similar vacuoles in a large diatom contain a lower proportion of the heavier ions than the surrounding sea water, a factor contributing to the buoyancy of these cells. In *Noctiluca*, vacuoles contain an acidic solution, indicating that Na^+, K^+, and possibly other positive ions may be replaced by H^+; the resulting change in density of the vacuolar solution could cause the organisms to float [9].

In many marine dinoflagellates, a special opening into the cell body, a pusule, occurs in the region adjacent to each point of flagellar attachment. The pusules each have a small pore-like hole and usually increase in diameter within the cell body, forming a sac-like structure with a narrow opening (figure 21). In some species, where flagella are attached at points distant from one another, the pusules are often elongated and interconnected (figure 22). The sac is filled with a fluid that is usually tinged pink. Pusules function in the absorption of water and according to Kofoid and Swezy [2], food particles are sometimes ingested through them. It also seems possible that they may function in flotation, perhaps in a manner similar to that of the large internal vacuoles.

The flagellar apparatus in large spherical-celled dinoflagellates, such as *Noctiluca*, is no larger than that in smaller ones, and it seems likely that the large cells are capable of only sluggish directional movements. *Pyrocystis* (figure 10) has no flagellar system except in reproductive stages; on the other hand, *Polykrikos* and *Phaeopolykrikos* (figure 11), are large cells with several flagellar systems. Individuals of these genera are single cells derived from several cells or, from another point of view, incompletely divided cells that have retained and even multiplied the flagellar apparatus without the usual complete division and separation of daughter cells.

The genera of unarmoured dinoflagellate cells are defined primarily on the basis of the fraction of cell volume behind the girdle groove. Cells with the larger part of the cell behind the girdle are in the genus *Amphidinium* (figures 6 and 23); those with the reverse pattern are designated *Katodinium* (figure 24); and if both parts are approximately equal, the cells belong in *Gymnodinium* (figures 7 and 20). A large number of species have an increase in the amount of space between the point of departure of the girdle and the point where it joins the sulcus. As a result, the girdle is displaced on the ventral side, descending in a spiral to the left of the cell. The trailing flagellum is often attached at the junction of the girdle end and the sulcus, and this point may be a considerable distance from the attachment of

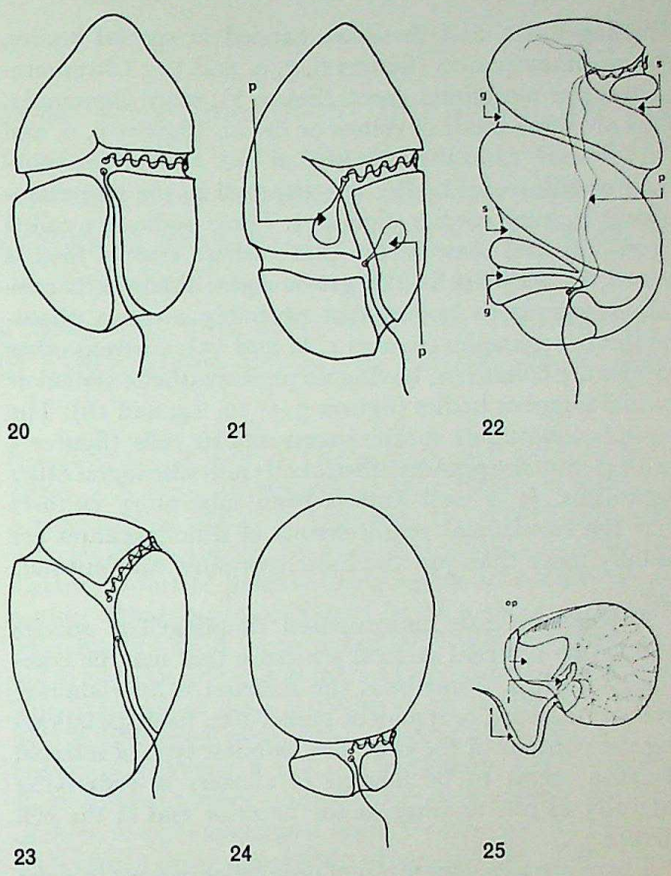

Figure 20 *Gymnodinium* (hypothetical).

Figure 21 *Gyrodinium* (hypothetical). p=pusules.

Figure 22 *Cochlodinium* (hypothetical, but similar to fig. 12). p=fused pusule channel, g=girdle, s=sulcus.

Figure 23 *Amphidinium* (hypothetical).

Figure 24 *Katodinium* (hypothetical).

Figure 25 *Noctiluca* (redrawn from Kofoid and Swezy). Lateral view. t=tentacle, f=flagellum, op=oral pouch. (×40 approx.)

the girdle flagellum at the forward end of the sulcus. Species with conspicuously displaced girdle ends are placed in the genus *Gyrodinium* (figures 4, 5, 8, 9, 16, and 21). There are intermediate species and forms, and the existence of these shows that the distinction between *Gymnodinium* and *Gyrodinium* is artificial.

Species having advanced girdle displacement often show a twist in the central part of the cell, leading to a displacement of the dorsal and ventral planes. In some species this may be extreme — there may be a twist of from two to four complete turns. All species showing this type of twist are placed in the genus *Cochlodinium* (figures 12, 13, 14, and 22). This includes several species in which the trailing flagellum is on the side of the cell opposite to the point of origin of the girdle flagellum.

Cell contents

The nucleus is a very conspicuous organelle in dinoflagellate cells and is often the largest. Dinoflagellate nuclei are quite distinct from those of most other types of cells, in that the chromosomes retain their condensed appearance throughout interphase [6, 7] when they can be clearly recognized as thickened, thread-like structures (figures 13, 14, 17, and 19).

There are often photosynthetic pigments (chlorophylls *a* and *c*, and various accessory pigments) in

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dinoflagellates, and these are carried in special bodies, the chromatophores (figures 6, 7, 9, and 13). Chromatophores are sometimes green (figure 7); more commonly, they are some shade of yellow or brown (figures 6, 9, and 13); in some cases they are blue or red. Colourless, spherical or ellipsoidal bodies are attached to the chromatophores in some species (figure 7). These bodies are called pyrenoids and may be the place where reserve food is stored, as they are in the green algae. Some cells contain pigments in bodies that probably are not photosynthetic organelles (figures 1, 8, and 15), whereas other species are colourless, having no photosynthetic system or special pigment bodies (figures 3, 5, 12, 14, and 16). The non-photosynthetic species ingest smaller cells (figures 5 and 14), and the photosynthetic cells may also ingest other organisms. It is well known from laboratory cultures that the nutritional requirements of dinoflagellates are usually more than just the basic inorganic nutrient salts [5].

A few very rare unarmoured dinoflagellate species contain an internal skeletal structure that may be composed of silica. Sometimes the skeleton is an elaborate stellate structure, or it may be basket-like, its shape following the contour of the cell. The simplest type of internal skeleton seems to be formed of clusters of rods lying laterally to one another at the anterior end of the cell (figure 3).

There are two very unusual organelles present in some species of unarmoured dinoflagellates, the cnidocyst and the ocellus. Cnidocysts are ejectile organelles, and are known in cells of *Polykrikos* and *Nematodinium*; in structure they appear to be very similar to the nematocysts of coelenterates, but their function in dinoflagellates is not known. Smaller ejectile organelles are known in diverse species of dinoflagellates [11], some, called muciferous trichocysts, emitting an amorphous, muciferous substance, and others, the fibrillar trichocysts, ejecting a fibrillar strand. K. E. Wohlforth-Bottermann [12] has suggested that the fibrillar trichocysts may be involved in the osmo-regulation system of the cell. J. Dragesco and A. Hollande studied fibrillar trichocysts with the electron microscope and showed [13] that they are located in the ectoplasm and arranged perpendicular to the cell membrane. In structure, they are very similar to the trichocysts of ciliate protozoa.

Five rarely observed genera are placed in a distinct family because of the occurrence of an ocellus, a simple single 'eye'. The ocellus is composed of two pieces, a translucent, colourless lens and a pigment body, usually black or red. The lens varies in size and shape and is often spherical (figure 17). Sometimes it is elongated and appears to be laminated (figure 19). The pigment body may appear in any position around the lens, and in some species, the pigment mass may be quite diffuse, occurring in joined strands located near the lens but not always attached to it. The small pigment body in figure 17 may not be in a functional state because the cell appears to be encysted. In most species, the ocellus is located in the rear half of the cell, and on the left side. Its function has not been experimentally demonstrated, but most authors infer, on the basis of its structure, that it acts in the orientation of the cell towards light. They are truly remarkable cell organelles from the point of view of their structure, and experimental analyses of the function of this body should be most interesting.

Primary productivity and dinoflagellates

The 'nanoplankton' that often contributes a major fraction of primary productivity in certain parts of the oceans consists to some extent of unarmoured dinoflagellates and very small armoured species. Most photosynthetic unarmoured dinoflagellates fall within the size range (5–90 μ) to which 55 to 72 per cent of the photosynthetic activity in the Indian Ocean has been attributed [14]. A small, photosynthetic *Gyrodinium* (figure 4) occurred at all of the the stations studying productivity in the Indian Ocean on the second cruise of the *Anton Bruun*, and at many, it was the most abundant of the photosynthetic phytoplankton observed. The species of *Gymnodinium* illustrated in figure 7 was also common in Indian Ocean samples, and these two species, in addition to several very small species of armoured dinoflagellates (in the genus *Oxytoxum*) that were common, may be responsible for most of the primary productivity in some areas of the Indian Ocean.

Most of the very strange unarmoured dinoflagellates are not abundant in phytoplankton samples, and are not important primary producers in the sea; and few, if any, of the cells with cnidocysts or ocelli have photosynthetic chromatophores. In addition a large proportion of armoured dinoflagellates are not photosynthetic, and estimates of productivity based on cell counts that include these species are unreliable. There is a great need for a survey of all dinoflagellate species from the point of view of their photosynthetic systems, because many armoured species from preserved samples are tabulated as being photosynthetic, but they have never been examined in the living condition for evidence of photosynthetic chromatophores.

Acknowledgments

This work was supported by the National Science Foundation as a part of the U.S. Program in Biology, International Indian Ocean Expedition. While conducting this research I was a member of the staff of the United States National Museum, Smithsonian Institution. I am indebted to Professor R. G. Dean, Oceanography Department, University of Washington, for his assistance in estimating the energy conserved by streamlined phytoplankton cells.

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The applications of neutron diffraction

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G. E. Bacon

Most of our knowledge of the structure of solids has come from X-ray diffraction, but this gives only poor information about the position of atoms that have few electrons: one of the more important of these is hydrogen. Neutrons are diffracted by nuclei and can easily 'see' hydrogen atoms. This article describes the applications of neutron diffraction to the study of chemical structures, including hydrogen bonds. Other applications arise because neutrons have a magnetic moment and can be used to map a 'magnetic unit cell'; and they can also give information about the vibrations in a crystal, and hence about the forces existing in a solid.

Regularity, symmetry, and uniformity are basic features of the architecture of solids, and arise because, for each chemical element from which the solid is constructed, all atoms are identical. We cannot observe individual atoms, in the sense in which we can see individual grains of fine sand in a microscope, but we can deduce indirectly the shape and size of the 'unit cell', that is, the smallest group of atoms out of which, by constant repetition in three dimensions, we can build up a solid. As well as the size and content of this cell, we can determine the locations of the individual atoms within it.

The analysis of distributions in time and space

In order to appreciate the rather indirect approach to the details of this unit cell, let us consider an analogy from musical sounds. The note middle C as produced in turn by a piano, a flute, and a violin sounds quite different, because the fundamental vibration is accompanied by harmonics and overtones that differ for the different musical instruments. If we measure the way in which the air pressure varies with time in the sound waves which are transmitted, we get curves like those in figure 1. The time interval over which each curve repeats itself is the same, represented by α in each figure, but the form of the variation over the interval in each case is quite different. In the case of our sound waves, we can disentangle these complicated shapes mathematically and show how they are composed of various combinations of simple sine curves: this is done in figure 2 for a particular example. Alternatively, we could have directly assessed the magnitude of the component curves *a*, *b*, *c*, *d*, *e* by making practical experiments with a set of resonators. Then, by combining these curves graphically we could have arrived at the complicated resultant variation of pressure that is represented by curve *f*.

The structure of a solid is periodic in space, for the solid is built up by repeating a unit cell in three dimensions. We can express the atomic content of a cell as a spatial distribution of either electron density, electric potential, or nuclear density, and any one of these quantities can be considered analogous to the pressure in the sound wave represented by curve *f*. We are able to discover the shape of this resultant curve, thus defining the 'cell content', by an experimental technique which measures the individual contributions of the component curves *a*, *b*, *c*, *d*, and *e*. The normal method is to use a beam of X-rays, an electromagnetic radiation having a wavelength of about 1 Ångström unit (10^{-8} cm): this wavelength is chosen because it is about equal to the distance apart of neighbouring atoms in a solid. If we project a fine beam of X-rays on to a small crystalline fragment of a solid, we find that the X-rays are scattered, not at random, but in a number of well-defined directions. The intensity of each secondary, or 'diffracted', beam that is produced represents a separate structural term comparable with *a*, *b*, *c*, *d*, or *e* in figure 2. If we combine these curves together—and there may be several hundred of them in our experiment with X-rays—we shall obtain a picture in three dimensions of the unit cell of our solid. This technique is known as structure analysis by X-ray diffraction, and it has been developed from the original work of M. von Laue, and Sir William Bragg and Sir Lawrence Bragg, in 1912. The purpose of the present article is to explain the advantages of using neutrons instead of X-rays in a similar technique. There are certain properties of neutrons that are particularly valuable and lead to important advances in our knowledge of the chemistry and physics of solids. The technique has some

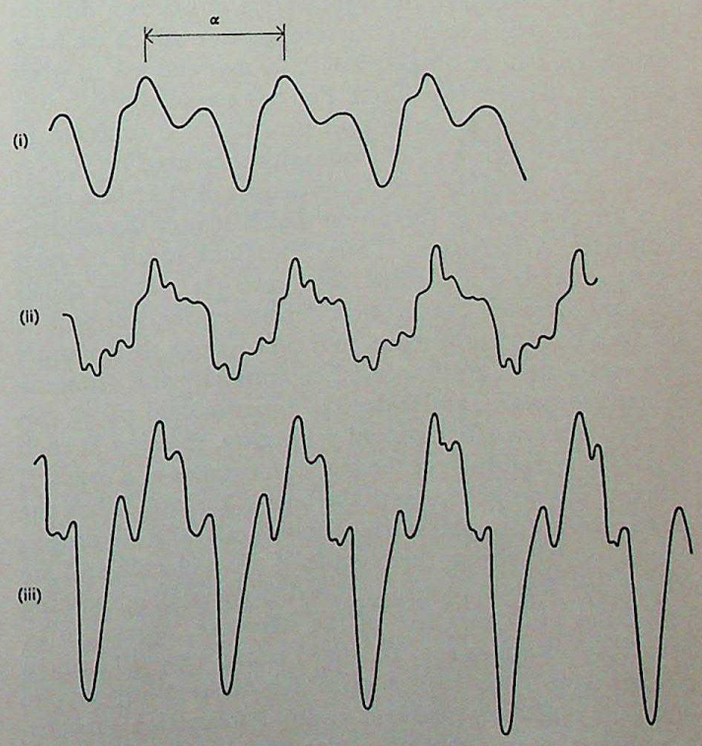

Figure 1 The way in which the pressure varies with time for the same musical note as played by (i) flute, (ii) clarinet, (iii) saxophone. (Based on data from D. C. Miller, 'The Science of Musical Sounds'. Macmillan, 1916.)

G. E. Bacon, *M.A., Ph.D., Sc.D., B.Sc., F.Inst.P.*
Was born in Derby in 1917 and educated at Emmanuel College, Cambridge. During the war he did research on ground radar systems for the Air Ministry. He joined the Atomic Energy Research Establishment, Harwell, in 1946, and pioneered the development of neutron-diffraction analysis in Britain. Since 1963 he has been Professor of Physics at the University of Sheffield.

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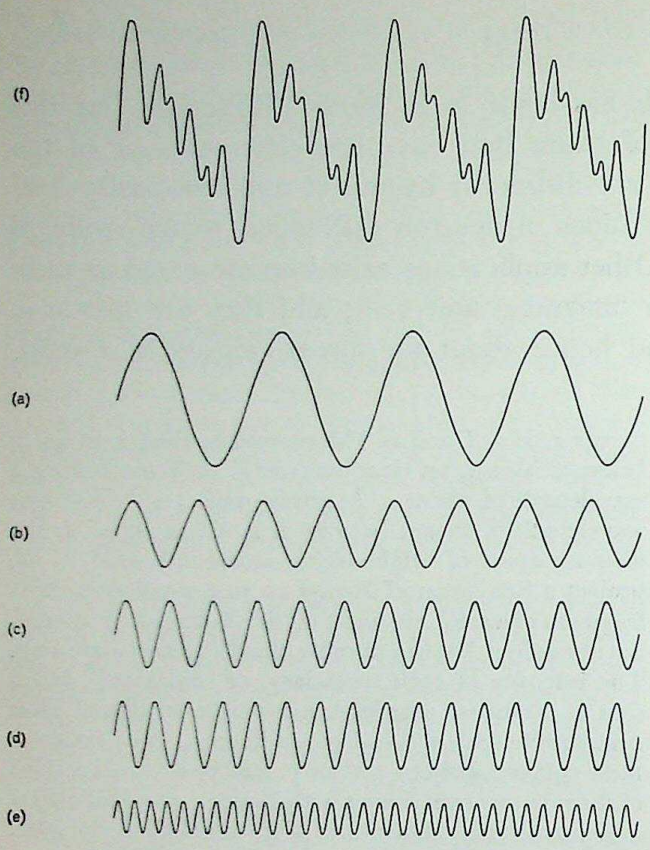

Figure 2 The composite pressure-time variation shown in the upper curve *f* is obtained by adding together the five fundamental vibrations represented by curves *a*, *b*, *c*, *d*, and *e*.

unique advantages which provide compensation for its unfortunate limitation: this is that a nuclear reactor is the only source of neutrons that is sufficiently powerful for the experiments.

In order to realize the significance of neutron diffraction, let us return to the structural picture which we have just shown can be obtained with X-rays and ask in what terms the picture is painted. For our sound waves it was the variation of pressure that provided the ordinate in the curves of figure 1. The quantity measured by X-rays in the unit cell of the solid is the density of electrons, since it is the electrons in the atoms which scatter the electromagnetic X-radiation. Thus, the final result of such measurements is a picture like figure 3(a), which shows the way in which the electron density varies over part of the unit cell in anthracene, and thus reveals the contours of a molecule of anthracene. For simplicity and economy of representation, and indeed of experimental effort, this picture is a two-dimensional projection, showing at each point the magnitude of the electron content of a unit cell when this is projected on to the base of the cell. It has one particularly disappointing limitation. The hydrogen atoms, which are on the outside of the molecule and are of primary importance in determining how neighbouring molecules pack together in the structure, appear to be relatively insignificant. It would prove very difficult to extract from their rather primitive outlines any precise knowledge of their positions or any information concerning their thermal motion about their equilibrium positions, although this could clearly be done for the carbon atoms. The reason for this inconspicuousness of the hydrogen atoms is simply that they contain only a single electron, in contrast to the six for the carbon atoms; and it is the electrons that the X-rays 'see'. As a more extreme example, we could consider attempts to detail the structure of uranium compounds, such as UH_3 or UO_2. An atom of uranium contains 92 electrons, so that even an oxygen atom, with its eight electrons, will be very difficult to discern alongside it. Alternatively, we may say that accurate location of the oxygen atoms would require that the measurements of the intensities of the scattered X-ray beams would need to be made much more accurately than can be achieved in practice.

How atoms scatter neutrons

The use of neutrons offers an opportunity of overcoming the limitations we have just described. Neutrons are uncharged particles, and because of this they penetrate solids extremely easily, so that for most materials a thickness of a centimetre reduces the intensity of a neutron beam by no more than a few per cent. Moreover, the electrons which occupy most of the volume of the atoms, and which are the prime agent in scattering X-rays play no part in scattering a beam of neutrons. The neutrons —monochromatic neutrons are actually used—continue through the electron cloud until they reach the nucleus, which behaves as an impenetrable object, and causes the neutrons to be diverted from their incident path to an extent that depends on the nuclear size. A large nucleus will scatter many neutrons, a small one will scatter only a few; but in either case the neutrons are scattered evenly in all directions. Neutrons possess some properties which are usually associated with waves, and it is the wave properties of a neutron beam that determine this even spatial distribution of scattered neutrons. It can be shown that for thermal neutrons—those which have energies about equal to those of atoms or molecules at ordinary temperatures—there is an effective wavelength of about 1 Å, much the same as that of the X-rays about which we have been speaking previously. The isotropic distribution of the neutrons scattered by a single nucleus arises because the dimensions of the latter, approximately 10^{-12} cm, are vastly smaller than the neutron wavelength of 10^{-8} cm. On the other hand, when we consider the scattering by the ordered arrays of nuclei that describe the appearance of a solid as viewed by neutrons, the fact that the wavelength is about the same as the distance of separation between neighbouring atoms will ensure that the neutrons are scattered only in a number of well-defined directions. This is in fact an interference pattern, and these directions are the ones in which the contributions of neighbouring atoms are superimposed. As in the case of X-rays, a measurement of the scattered intensity in each of these directions will provide one of the terms, such as *a*, *b*, *c*, *d*, and *e* in figure 2, from which we build up our picture of the structural unit in the solid.

Let us now consider the way in which atoms of different chemical elements will scatter neutrons. As we have seen already, the determining factor is the physical size of the nucleus. It can be shown that the amplitude b of the scattered beam is proportional to the cube root of the mass number (A) of the nucleus, and therefore increases only quite slowly as we choose heavier nuclei. For example, the actual values of b for atomic mass numbers of 10 and 200 are $0{\cdot}33 \times 10^{-12}$ and $0{\cdot}90 \times 10^{-12}$ cm respectively. Thus we have a ratio of only about 2·7 between these two atoms, in contrast to a ratio of about 18 for their

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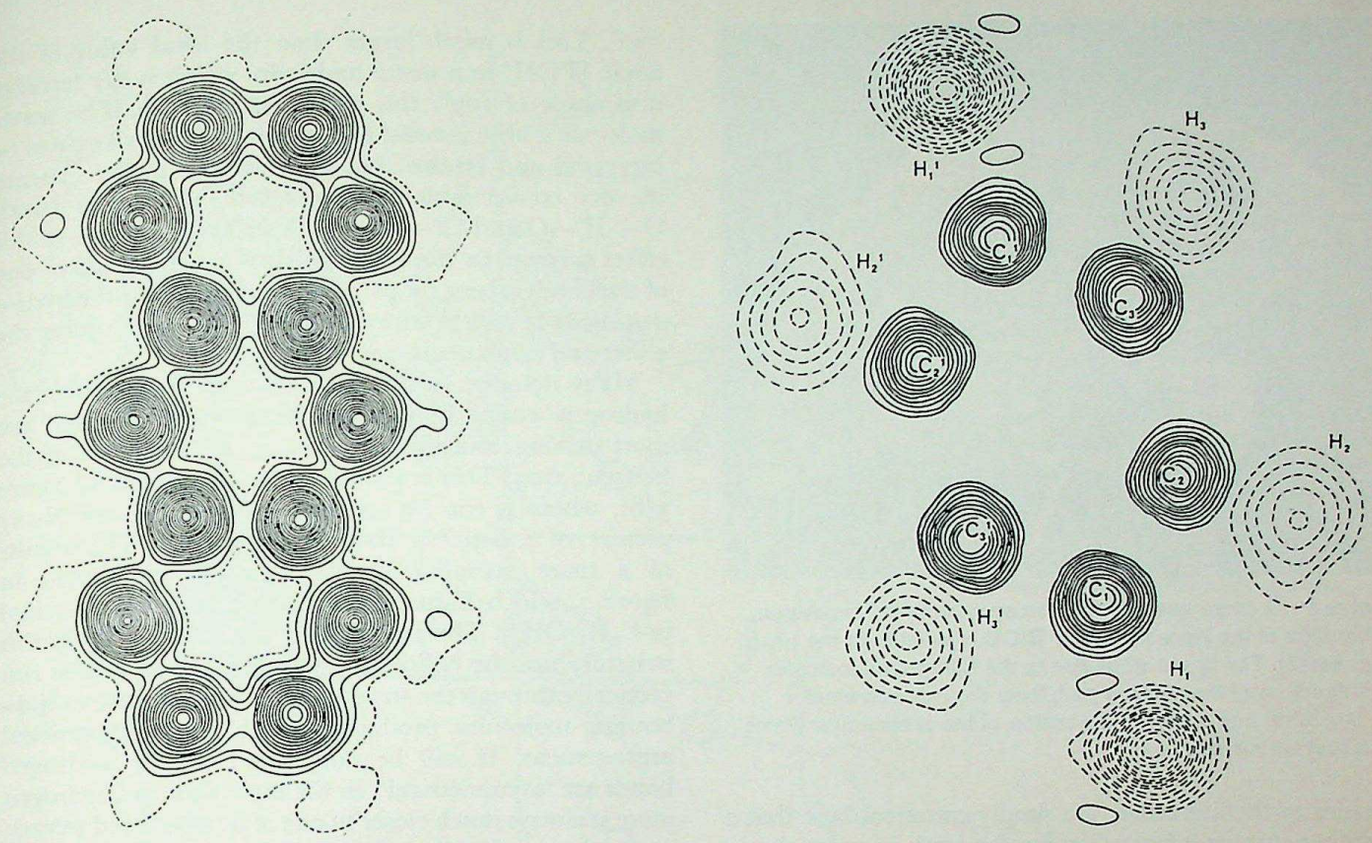

(a) (b)

Figure 3 A comparison of the relatively insignificant detail of the hydrogen atom revealed by X-rays in an anthracene molecule (a) with the full detail provided by neutrons for the benzene ring in solid benzene itself (b). The larger scattering density at H_1, H_1' in (b) occurs because pairs of hydrogen atoms overlap in the projection. ((a) is based on U. C. Sinclair *et al. Acta Cryst.*, 3, 251, 1950.)

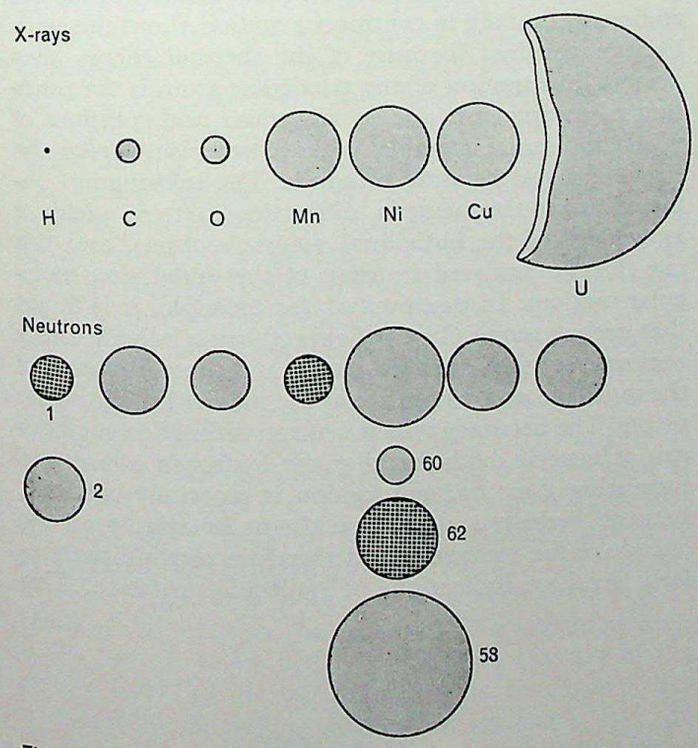

Figure 4 The visibilities of some important atoms for X-rays and neutrons. The cross-hatched atoms have negative amplitudes in neutron scattering.

powers of X-ray scattering. It will be seen, therefore, that the prospects for distinguishing and locating 'light' atoms in solids are vastly improved when neutron beams are used. Before considering some specific examples, let us examine a second feature of the scattering process which is of great importance in particular cases. Certain nuclei produce preferential scattering on account of a resonance process which depends on the permissible values of energy which may be present in the nucleus or, more correctly, in the compound nucleus which we imagine to be formed temporarily from the target nucleus and the neutron. The processes have recently been described in ENDEAVOUR by Sir Harrie Massey [1]. A consequence of this is that the scattering due to the nuclear size effect may be reinforced, or sometimes diminished, by this resonance scattering. The resonance scattering varies in a seemingly haphazard way from element to element, and is sometimes markedly different even for different isotopes of an element. As a result, our picture of a slow, but steady, increase of visibility with increase of nuclear mass has to be modified by these rather random fluctuations. The practical situation is illustrated in the lower part of figure 4, which represents the 'visibility', in neutron diffraction experiments, of the nuclei of various elements and, in some cases, of their different isotopes. In marked contrast we also show in figure 4 how the visibility of atoms in X-ray diffraction experiments increases steadily with atomic number. In order to realize the full implications of this discussion it would be necessary to examine a complete table of values of scattering amplitude b for all the elements and isotopes which have been investigated: such a table can be found in reference [2]. However, the information which is displayed in figure 4 represents some important cases and will be sufficient to permit an understanding of several typical examples of applying these techniques to some chemical problems which we shall now describe.

For a practical description of the way in which the experimental measurements are carried out we refer the

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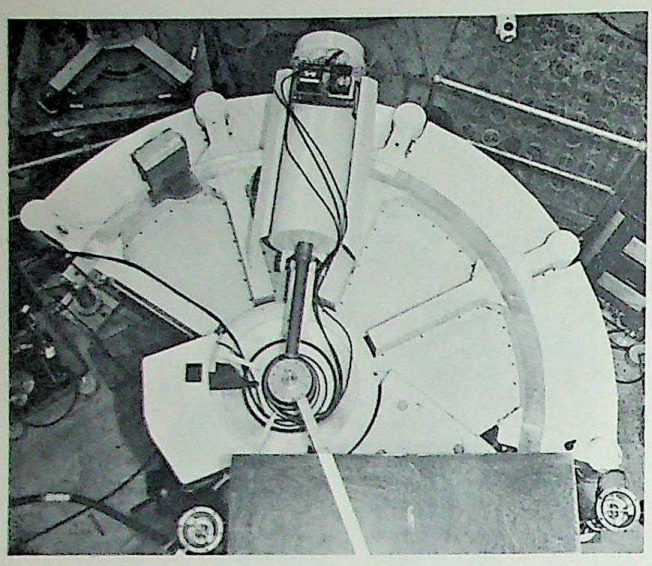

Figure 5 A large general-purpose spectrometer for neutron diffraction at the Harwell reactor DIDO, viewed from the top of the reactor. The broad white line in the foreground indicates the direction of the neutron path from the monochromator to the diffracting sample. The radius of the semicircular frame is about 1·5 metres.

reader to the literature. We simply comment here that a nuclear reactor is necessary for the work in order that a neutron beam of adequate intensity shall be available (figure 5). Indeed, in order that the most worthwhile measurements can be made it is essential that the reactor should yield not less than 10^{13} neutrons passing per second through a square centimetre. This restriction limits the full development of these methods to a rather small number of laboratories throughout the world.

Locating hydrogen atoms

A wide range of chemical compounds, both inorganic and organic, has been judged to contain hydrogen bonds. These can be of either an intramolecular or an intermolecular nature, binding together either different groups within a molecule or neighbouring molecules. In the latter case, for example, oxygen atoms in neighbouring molecules may be brought unusually close together through the agency of an intervening hydrogen atom. In order to interpret the details of this kind of bonding it is essential to know the precise position of the hydrogen atom between the two oxygen atoms. This can be found out very much more accurately and directly by neutron diffraction than by any other method, and some of the earliest applications of the technique were to hydrogen-bonded substances. As examples we may mention some studies of hydrated compounds, from which it was fully realized for the first time the way in which these structures are held together by hydrogen bonds between the molecules of water of crystallization and oxygen atoms in the anions. The alums—a typical formula is $K_2SO_4.Cr_2(SO_4)_3.24H_2O$—copper sulphate $CuSO_4.5H_2O$, and sodium sesquicarbonate $Na_2CO_3.NaHCO_3.2H_2O$ are among the hydrates which have been examined in this way. The detailed results indicate the remarkable strength of the water molecules in resisting distortion by the surrounding atoms. A typical environment is illustrated in figure 6 where, for one of the water molecules in copper sulphate, the layout of the neighbouring groups of atoms is such that the angle O′OO″ is equal to about 130°. This is much larger than the ideal value of the angle H′OH″ in a water molecule, which is the tetrahedral angle of 109°: this occurs in solid ice. The water molecule is able to resist any tendency for this angle to be increased and retains the value of 109° at the expense of very considerable bending of the hydrogen bonds O′—H′—O and O″—H″—O. A striking example of this effect is found in the hydrate $MgSO_4.4H_2O$, where one of the bonds is bent by 40°, with the result that the hydrogen atom is 0·44 Å away from the line which joins the water and sulphate oxygen atoms [3].

Many detailed studies have been made to locate the hydrogen atoms in organic compounds. Perhaps the most striking, and simplest, case is the structure of the benzene ring. This is shown for solid benzene in figure 3(b), where it can be contrasted directly to the X-ray picture of a benzene ring in anthracene. The results of a more complicated investigation are shown in figure 7, which illustrates the structure of α-resorcinol m-$C_6H_4(OH)_2$. The most interesting features [4] of this structure are the helices of hydrogen bonds. These run vertically through the structure and bind together neighbouring molecules, producing a rigid three-dimensional arrangement. It will be noted that all the hydrogen bonds are 'asymmetrical', in the sense that the hydrogen atom is always much closer to one of its associated oxygen atoms than to the other. A second feature of the structure comes out plainly from the neutron diffraction data, although it is not immediately apparent from figure 7. This figure, like figure 3(b), is only a static representation of the structure, and indicates the average or equilibrium positions of the various atoms. In fact, the atoms are not stationary, but are in continuous motion about the equilibrium positions, because of the thermal energy they possess. The motion of any particular atom is the resultant of components due to vibrations and rotations of whole molecules together with those arising from the stretching and bending of bonds. The information obtained from the neutron diffraction pattern yields a knowledge of the individual atomic motions, and this can then be analysed in terms of the underlying molecular motions. In α-resorcinol, for example, it is found that carbon atoms C_4, C_6 (figure 7) are relatively firmly anchored by the hydrogen bonds, and there is motion of the molecule as a whole about the axis which joins these pivots. The accuracy which neutron diffraction methods can achieve in both locating the hydrogen atoms and measuring their thermal motion is especially valuable, because hydrogen atoms are almost invariably on the outside of the molecules and therefore provide particularly sensitive indications of molecular rotation. This

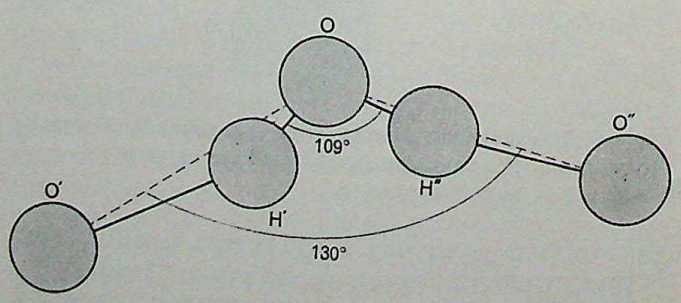

Figure 6 The environment of a water molecule in hydrated copper sulphate $CuSO_4.5H_2O$, showing the bent hydrogen bonds.

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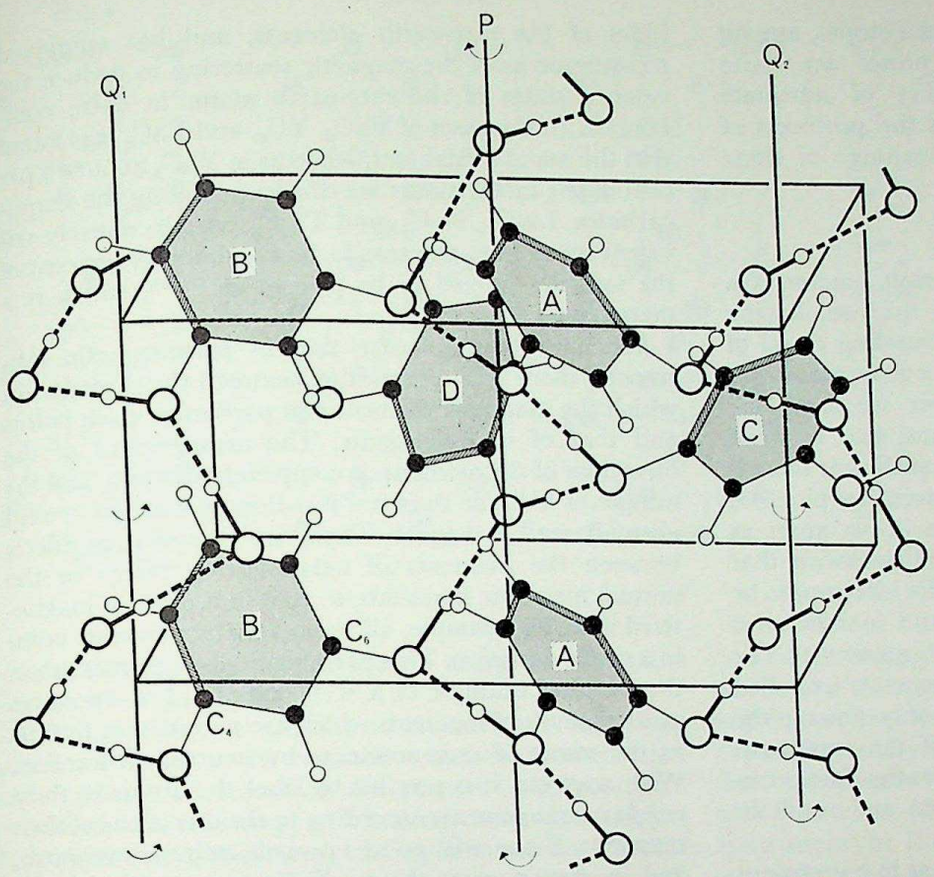

Figure 7 The structure of α-resorcinol, showing the helices of hydrogen bonds. A, B, C, D are the four molecules contained in a unit cell and A′, B′ are corresponding molecules in the cell above. The atoms are indicated as Carbon ● Hydrogen ○ Oxygen ○ and the benzene ring is drawn solid and shaded to simplify identification. The OH groups in these molecules are linked together by the spiral of hydrogen bonds, drawn in heavy line, which goes around the vertical axis P drawn through the centre of the unit cell. Similar spirals, but of opposite hand, through the vertical edges of the unit cell link the molecules to those in neighbouring cells: two of these spirals, around the vertical axes Q_1, Q_2, are drawn in the figure, incorporating OH groups from some of the molecules in neighbouring cells.

point is well illustrated by a study of the structure of hexamethylene-tetramine [5]. This molecule is roughly spherical in shape, with outwardly directed hydrogen atoms, and an assessment of their large motion provided an accurate measure of its oscillations.

Before leaving the problem of locating hydrogen atoms, let us mention a very unusual feature indicated in figure 4. Deuterium is substantially more visible than hydrogen itself and, so far as neutrons are concerned, deuterium is a very good example of the 'average atom'. This means that the accuracy and discrimination of our methods will be substantially increased if we can use deuterated material instead of ordinary hydrogen-containing samples. It also follows that when deuteration takes place only for particular hydrogen atoms in the molecule, these hydrogens will be immediately obvious in the structural pictures obtained by neutron diffraction. This has been demonstrated very plainly with pentaerythritol $C(CH_2OH)_4$ [6]. The distinction between H and D is even more outstanding than might appear at first sight. As figure 4 shows, deuterium scatters substantially more neutrons than does ordinary hydrogen: in addition, the scattering amplitude is of the opposite algebraic sign. This is the outcome of a difference of phase of 180° between the incident and scattered neutron waves, which arises because of certain features of the energy levels in the two nuclei. As a result, ordinary hydrogen atoms appear as negative scatterers, and this of course reveals them even more strikingly among oxygen and carbon atoms in the typical environment of an organic compound. Deuterium atoms are positive scatterers, according to the usual conventions.

Other chemical applications

Let us now look briefly at the application of X-ray diffraction analysis to the other end of the Periodic Table from hydrogen. A task of some importance here is to elucidate the structural chemistry of the actinide elements and their compounds. A typical problem is the classification of the nature of the various phases which occur in the uranium-oxygen system, which is important in the development and study of fuels for nuclear reactors. The task of defining the various non-stoichiometric and defect phases which occur here is inherently difficult, but it is made vastly more so by two limitations of the X-ray method. Firstly, the absorption of these materials for X-rays is troublesomely high, and secondly, the scattering power of the oxygen atoms is quite insignificant compared with that of the uranium atoms. Neither of these restrictions exists for beams of neutrons, and very important progress is now being made, for example by B. T. M. Willis [7], in the study of these and related compounds. In particular, information is forthcoming about the precise relationship of the non-stoichiometric structures to the idealized structure of UO_2, and about the anisotropic motions of the atoms which occur.

In all the examples discussed so far, the value of using neutrons has depended on the broad equality among atoms of different elements as scatterers of neutrons. We mentioned earlier that a full list of scattering amplitudes for elements and isotopes would reveal some rather haphazard variations, and we should now like to comment on one or two of these. One particular example can be appreciated by referring once again to figure 4. In the iron group of transition metals, the elements Mn, Fe, Co, Ni, Cu are difficult to distinguish with X-rays because they differ successively by only one electron. The problem of distinguishing between them is an important one in the study of alloys and of compounds of technological interest, such as the ferrites. For neutrons, iron and nickel remain rather similar, but there are extremely large differences among the other members of the family, and distinctions can readily be made. Indeed, differentiation is very easily possible, in principle,

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even for Fe and Ni, by using separated isotopes, among which the variations in scattering power are quite remarkable. However, the availability of adequate quantities of separated isotopes limits the prospects of what can be achieved by taking advantage of these variations.

Magnetic scattering

We have emphasized that the scattering process is a nuclear one, in which the uncharged neutron, having penetrated without difficulty the surrounding cloud of electrons, interacts with the nucleus. For most atoms this is a fair and complete picture. However, we must look further at the case of 'magnetic' atoms, that is, those atoms whose outer electron structure is such that there is a resultant magnetic moment on the atom. In pictorial terms we may think of each electron in an atom as possessing a spin that is clockwise or anticlockwise, that is, positive or negative. The tendency is for electrons to be 'paired', with the result that atoms and ions in most solids do not possess overall magnetic moments. The exceptions, which do have a resultant moment, are called 'paramagnetic', and are found commonly among the transition metals and the elements of the rare-earth series. In certain circumstances, co-operative forces can arise between such paramagnetic atoms and result in ferromagnetism or antiferromagnetism.

The significance of paramagnetic atoms in our present discussion arises because the neutron, although it possesses no resultant electrical charge, possesses nevertheless a magnetic moment. This magnetic moment is very small, amounting to only about one-thousandth of the moment associated with a single unpaired electron, but it causes additional scattering when a beam of neutrons is incident on a magnetic atom. If we regard our incident beam of neutrons as a stream of very weak microscopic magnets, we can consider the extra scattering as due to an interaction between these magnets and the resultant magnetic moment of each paramagnetic atom. The quantitative value of this interaction was first calculated by O. Halpern and M. H. Johnson [8], who showed that the number of extra neutrons scattered by this process was proportional to $S(S+1)$, where $2S$ is the magnetic moment of the atom expressed in units of the Bohr magneton. In practice, values of $2S$ of a few units occur, and in these circumstances the additional contribution to the scattering amplitude because of magnetic scattering is about 10^{-12} cm. It is therefore very close to a typical value of nuclear scattering amplitude. We find therefore that the magnetic scattering is sufficiently intense to be observed and measured quite accurately by practical experiments. This leads to a vast extension of the field of neutron-diffraction studies. They can be applied to the determination of the distribution of magnetic moment in solids, not only to the problem of determining its distribution and magnitude within individual atoms, but to discovering such features as the detailed magnetic architecture of solids and the way in which magnetic materials are influenced by the addition of non-magnetic atoms. Most of this work is of more fundamental interest to physicists than to chemists and, as such, contrasts with most of the applications of nuclear neutron scattering. However, one series of experiments related to a chemical problem is worth particular mention. M. Atoji [9] has studied an extensive series of dicarbides and sesquicarbides of the rare-earth elements, and has employed measurements of the magnetic scattering to deduce the valency states of the rare-earth atoms in these compounds. In the cases of TbC_2, YC_2, and LaC_2 it is found that the metal is trivalent, whereas in YbC_2 about 17 per cent of the metal atoms are divalent. Among the sesquicarbides, La_2C_3, Pr_2C_3, and Tb_2C_3 contain entirely trivalent metal ions, whereas in Ce_2C_3 about 35 per cent of the ions are judged to be present as Ce^{4+}, which is a diamagnetic ion.

We have to emphasize that in paramagnetic substances, there is no correlation between the direction in which the magnetic moment of a particular atom points and that of its neighbours. The arrangement of the directions of the moments is completely random, and the sample as a whole does not function as what we would normally call a magnet. There are co-operative effects between the moments of neighbouring atoms in the normal magnetic materials, so that in a piece of magnetized iron, for example, all the magnetic moments point in a single direction. This particular case is no more than the simplest example of a wide variety of co-operative arrangements of moments which are now known to exist as the result of measurements by neutron diffraction. With neutrons it is possible to label the atoms in these regular arrangements according to the directions of their moments. Some will point upwards, some downwards, and in certain cases there will be moments at precise intermediate angles. We find that there is a 'magnetic unit cell' in the structure, in just the same way as we spoke of the ordinary chemical cell. Figure 8 shows in diagrammatic form some of the types of magnetic architecture which neutron diffraction has shown to exist. The discovery and subsequent detailed description [10] of these varieties of co-operative magnetism probably rank as the most significant achievement of neutron diffraction techniques so far. It is fair to say that as direct observers of magnetic moments, neutrons possess no rivals.

Inelastic scattering

In the foregoing account of the achievements of neutron diffraction we have restricted this term to the use of neutrons for determining the details of the repeating units that build up the regular structure of solids. We have, without mentioning the fact, been observing only those neutrons whose energy was not altered as a result of the scattering process, and it is observation of these particular neutrons which gives us the structural information which we have described. It is possible, however, for scattering collisions to take place which are 'inelastic', and in these circumstances the neutrons will gain or lose energy as a result of the scattering process. The most direct experiment is one in which a beam of neutrons is scattered by a single crystal and the directions and energies of the neutrons after scattering are measured. When there is a loss of energy, this is transferred, as a quantum process, to the crystal and results in the excitation of vibrations in the crystal. Calculation shows that the size of a quantum of crystal energy is of the same order as the energy possessed by the incident neutrons, roughly $10^{13}h$, where h is Planck's constant. This means that it is easy to measure the change in neutron energy sufficiently accurately to deduce the energy of the crystal vibrations. With X-rays, on the other hand, such a measurement is not practical, because the incident X-ray has an energy which is

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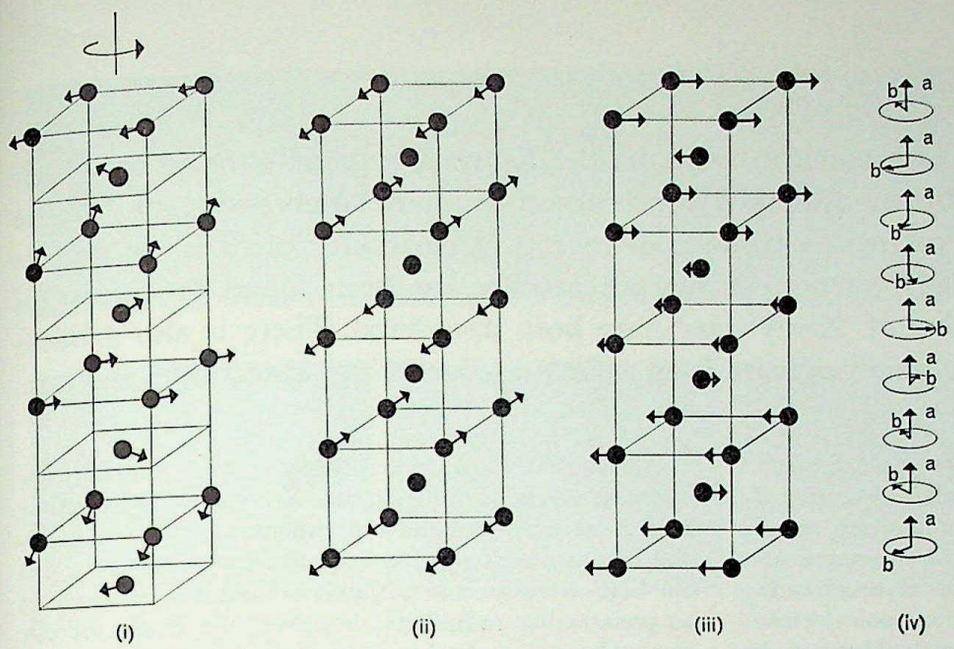

Figure 8 A diagrammatic representation of some of the kinds of co-operative magnetic arrangement which have been found by neutron diffraction. (i) A spiral arrangement of magnetic moments; (ii) standard antiferromagnetism; (iii) antiferromagnetism with sinusoidally varying moments; (iv) a 'composite' in which the magnetic moment for each plane of atoms is the resultant of a constant upwards component (a) and a horizontal spiral component (b).

100 000 times greater, and any loss of energy by inelastic scattering will be negligible.

With neutrons it is possible to measure not only the transfer of energy to the crystal but also the momentum and direction of travel of the phonon (the particle associated with the energy of vibration) that is produced. A combination of the energy and momentum data then enables us to construct the 'dispersion law' for the crystal vibrations—the dependence of the velocity of these vibrations on their frequencies. In an effectively continuous medium, such as air, the velocity is constant and the wave frequency is proportional to the reciprocal of the wavelength; but this is not the case for the vibrations in a crystalline solid. The detailed dispersion law is determined by the type of forces that exist in solids, and any theories of their nature can be tested against the data which are provided by the neutron experiments. For example, it can be shown that if one follows the assumption that forces between atoms are purely along the lines joining their centres, and dependent on the distance between these centres, one reaches the highly improbable result that in some crystals interactions must extend to at least the fourteenth neighbours. It seems clear that other types of non-central forces are required. Over the last few years a wide range of solids, including metals, alloys, semiconductors, and ionic crystals, have been studied in this way. Typical examples of the many materials which have been examined are aluminium, beryllium, sodium, β-brass, silicon, germanium, KBr, NaI, and graphite. The reader who wishes to study this work in detail is referred to a recent review article [11].

The crystal vibrations which we have just discussed define the way in which a disturbance spreads through a solid when an atom is displaced from its equilibrium position. In an ordered magnetic solid of the kind we have mentioned earlier there will be a corresponding propagation of magnetic disturbance when the magnetic moment carried by an atom is displaced. These disturbances, or 'spin waves', can be studied in an analogous way with neutrons by examining that part of the inelastic scattering which is magnetic. In this way it has been demonstrated that, whereas for low-frequency waves in antiferromagnetic materials, the dispersion law is linear, it is of quadratic form for ferromagnetic materials. Among the materials which have been examined are Fe_3O_4, $Co_{0\cdot92}Fe_{0\cdot08}$, α-Fe_2O_3, and MnF_2. At higher temperatures, the main application of these techniques is to study the critical scattering which occurs in the neighbourhood of the Curie temperature, above which the ordered magnetic arrangements break down. Here again the interested reader must be referred elsewhere for a full account [12].

Our aim has been to show, by choosing some of the simplest examples, the way in which detailed and quite unique information concerning solids can be obtained from experiments with neutron beams. As the intensities of available neutron beams have increased during the past twenty years, the applications of these experiments have extended to investigations over the whole field of atomic distributions and atomic forces in both solids and indeed liquids. With further prospective improvements in neutron fluxes it seems likely that this general field of research will continue to expand.

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X-ray astronomy

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Talbot A. Chubb

X-ray astronomy—the study of astronomical bodies by the X-rays they emit—started only after the second World War. This is because the radiation is absorbed by the atmosphere, and can be observed only with instruments carried by balloons or rockets. This article describes the present state of the study. An important fraction of sunspot activity has been found to consist of X-rays, and in addition, a number of 'X-ray stars' have been discovered. There is also a background of diffuse X-rays which may originate from near the edge of the observable universe.

X-ray astronomy is the study of astronomical objects through their emission of X-rays. As such, it is necessarily the study of high-energy processes in the universe, as only processes capable of heating objects to temperatures of the order of a million degrees, or of accelerating electrons to energies of at least the order of 1000 electron-volts, can produce X-ray emission. Even the bluest of the stars that are seen from the Earth are far too cold to produce measurable X-ray fluxes from their luminous disks, as the hottest of these objects is about 100 000 °K. One might therefore well conclude that there should be no field of X-ray astronomy. Nevertheless, there are easily measurable fluxes of cosmic X-rays, and they provide a valuable tool for gaining new insight into processes active in the universe.

Solar X-rays

If one were to seek a point in history at which X-ray astronomy was born, it would almost certainly be the moment when W. Grotian, who was followed by B. Edlen [1], first demonstrated the character of the solar corona. Before Lyot Coronographs, which provide an artificial eclipse, came into use, the solar corona was visible only at times of total eclipse, and until the 1930s it remained a total mystery. Indeed, there was doubt in the last century as to whether it was a real physical object, or only an optical effect produced by the Moon.

Toward the end of the last century coronal light was analysed spectroscopically and spectral lines were recorded. These showed that the corona was real, but raised a new problem: they did not correspond to emissions from any known element. It was Edlen who identified most of these mysterious lines. He showed that the strongest visible coronal lines were emissions from iron that was nine and thirteen times ionized (Fe^{X} and Fe^{XIV}). These studies paved the way for a description of the corona as a tenuous, almost totally transparent gaseous envelope, at a temperature of 10^6 °K, surrounding a much cooler Sun. Improbable as it seemed, iron could exist in such an electron-deficient form only in a medium of this type. Moreover, this model explained other observed phenomena—the polarized quality of the corona's pearly light, which is produced by electron scattering of sunlight, and the great height to which this scattering medium extends beyond the edge of the Sun. The production of X-rays is implicit in Edlen's model.

T. A. Chubb, *Ph.D.*

Was born in 1923 in Pittsburgh, and educated at Princeton University and the University of North Carolina. He has been carrying out astronomical measurements from rockets for about fifteen years at the United States Naval Research Laboratory, studying mainly far ultraviolet and X-ray emissions from the Sun and from celestial sources in the night sky.

Although Edlen's great discovery was made in the 1920s, it was not until 1949 that X-ray astronomy can be said to have begun as an experimental study. The essential device which was required to make it a reality was the high-altitude rocket. X-rays are normally thought of as penetrating radiations; however, the extent of our atmosphere is such that even the most penetrating of extra-terrestrial X-rays can be detected only with instruments carried in balloons: the lower energy—longer wavelength—X-rays produced by the Sun's corona are stopped at about the 100 km level. This is why rockets must be employed. The first experiments used V-2 rockets confiscated after World War II, and this laboratory, the United States Naval Research Laboratory, was one of several institutions that provided instrumentation for them. Solar X-rays were directly measured for the first time from these rockets, possibly by T. R. Burnight [2, 3] in 1948 using film, and certainly by H. Friedman, S. W. Lichtman, and E. T. Byram [4] in 1949. The latter used Geiger counters directed through a port in the nose cone of a V-2 rocket.

The study of solar X-rays continued throughout the 1950s, mostly using Geiger counters mounted on Aerobee rockets, and led to some surprising results. It was found that the fluxes measured in 1953 and 1954 were strikingly less than those observed in 1949. The high level that had initially been found reappeared only during the sunspot maximum of 1958 and 1959 [5]. Just as the corona brightens with sunspot activity, so does the flux of X-rays. Even more interesting than the general rise and fall of X-ray emission with the sunspot cycle has been the detailed study of X-ray emissions during solar flares. Flare X-rays were first detected from rockets in 1956 [6], and in 1958 a penetrating component of X-rays of about 100 keV was shown to appear in occasional bright flares [7, 8].

In 1960, observation of solar X-rays from artificial satellites began. These measurements showed that X-ray fluxes increase strongly during major flares, and also during other classes of activity, such as strong prominence activity and major expulsions of solar material [9]. They also showed that solar X-rays affect the Earth; they proved to be the cause of the fading of short-wave radio reception in the temperate zone that frequently occurs during sunspot maxima. Such fadeouts occur with striking suddenness and last typically for periods of ten minutes to an hour, and were previously known to be associated with solar flares. However, it was not known whether they were caused by a burst of ultraviolet radiation accompanying the flare or one of X-rays.

An experiment to discriminate between these is shown in figures 1 and 2. Figure 1 is a series of photographs of

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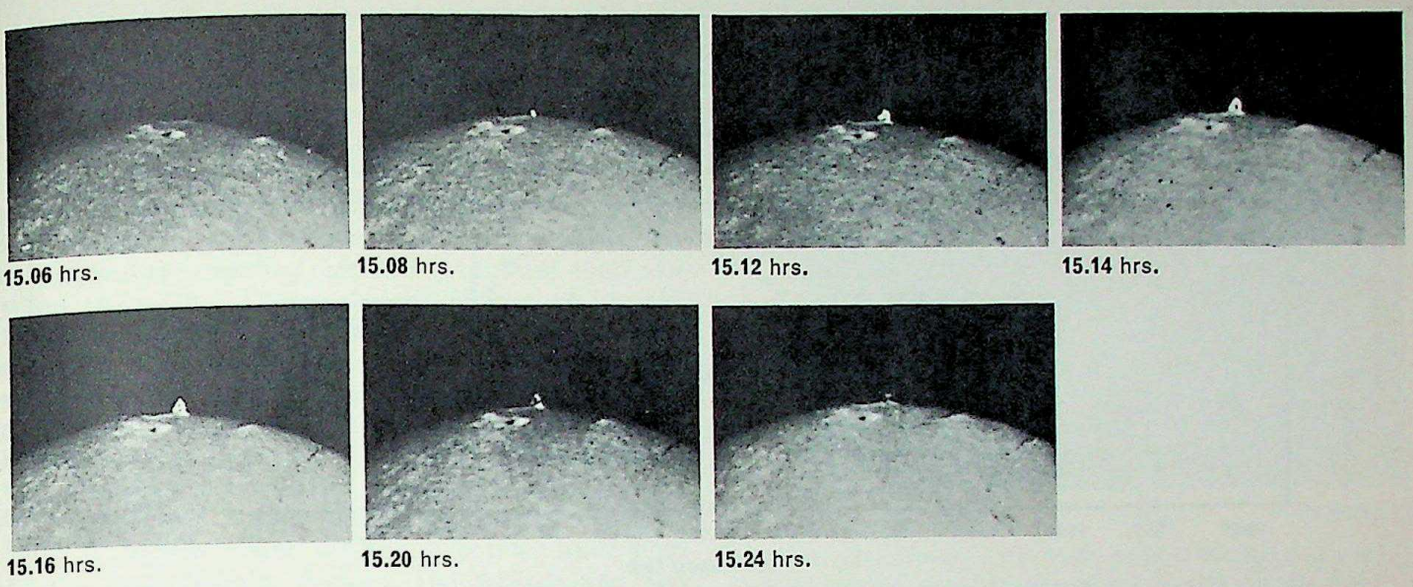

Figure 1 Photograph of solar disk in hydrogen alpha light, showing the development of a small limb flare on 6th August 1960.

the Sun's emission of hydrogen alpha lines, made by H. Smith from the Sacramento Peak Solar Observatory. When the Sun is observed through a very narrow band-pass filter centred on the red hydrogen alpha-line, one sees, not the main white disk of the Sun, but instead a network of overlying gas layers, some of which are locally brightened by solar-activity phenomena that are little understood. A strong local brightening of this high-altitude structure is called a solar flare: figure 1 shows such a flare developing on the limb of the Sun. This small flare is in the form of several bright arches. The flare developed rapidly in the period between 15.08 GMT and 15.12 GMT, and began to decrease in intensity after 15.16 GMT. Instruments in the satellite continuously recorded the intensities of both solar X-rays and solar ultraviolet radiation, and transmitted these data to ground each time the satellite passed overhead. The data are shown in figure 2.A small flux of X-rays of a wavelength of 1–8 Å was already striking the satellite when it first reached data transmission range. This flux grew by a factor of 5 during the period 15.10 GMT to 15.12 GMT, the period of most rapid flare development. Solar ultraviolet, on the other hand, continued at its normal steady level, increasing five per cent at the most. The large percentage increase in X-rays as compared with the relative constancy of ultraviolet radiation clearly implies that the radio fade-out and other ionospheric disturbances observed on the Earth during the flare were caused by the increase in X-rays and not by the ultraviolet radiation.

Solar X-ray astronomy is still in its formative stages, although X-ray photographs of the Sun have been made by several research groups [10–12]. These photographs show that solar X-rays come from small regions of local activity on the Sun, the same regions that have sunspots. In X-ray photographs the Sun has a very splotchy appearance. Another method of investigation is solar X-ray monitoring, which is carried out on a more or less routine basis—several bands of soft X-ray emissions are recorded semi-continuously. The emissions serve as sensitive indices of solar activity. At present, solar X-rays are received by photometers in the Explorer xxx satellite, which immediately transmits the data to Earth. These data are recorded by the NASA (National Aeronautics and Space Administration) network, for use primarily by scientists in the United States, and also by scientists at solar observatories in many other countries. An especially interesting use of these data was made by M. Landini, D. Russo, and G. L. Tagliaferri [13], and by L. Thomas, F. H. Venables, and K. M. Williams [14], who observed the attenuation of solar X-rays at sunset and sunrise passings of the satellite. Both groups used these attenuations repeatedly to measure the density of the Earth's atmosphere at the 150 km level.

We can expect an increasing understanding of the physics of solar activity to come from increasingly subtle X-ray astronomy studies. Already spectra have been obtained in the 12–25 Å region [15], where emissions from oxygen atoms that have lost six and seven electrons, and from iron atoms that have lost sixteen, have been identified. Eventually it will be possible to record the full X-ray line spectrum of the Sun and to establish more reliable quantitative information concerning the composition of the corona. It will also be possible to study spectral changes accompanying the development of regions of activity and of flares. We should be able to study the formation of high ionization states in iron and to distinguish the spectrum produced by the injection of high-energy electrons into 'cold' solar gas from the spectrum produced by local plasma heating. Such studies, combined with high-resolution X-ray photography, should help us to understand the causes of solar events and the mechanism that heats the corona.

Stellar X-rays

Although the detection of solar X-rays was predictable, the discovery of X-ray stars was not expected. Despite this, X-ray sky scans using relatively insensitive equipment were carried out as early as the late 1950s, but they failed to find any X-ray source. However, in 1962 sensitive equipment was used by R. Giacconi, H. Gursky, F. R. Paolini, and B. B. Rossi to look for X-rays produced on the Moon [16]. The experiment was a failure as far as detection of lunar X-rays was concerned, but a far more exciting discovery was made: X-rays from the general region of the galactic centre were observed.

We now know that there was a small error in the initial

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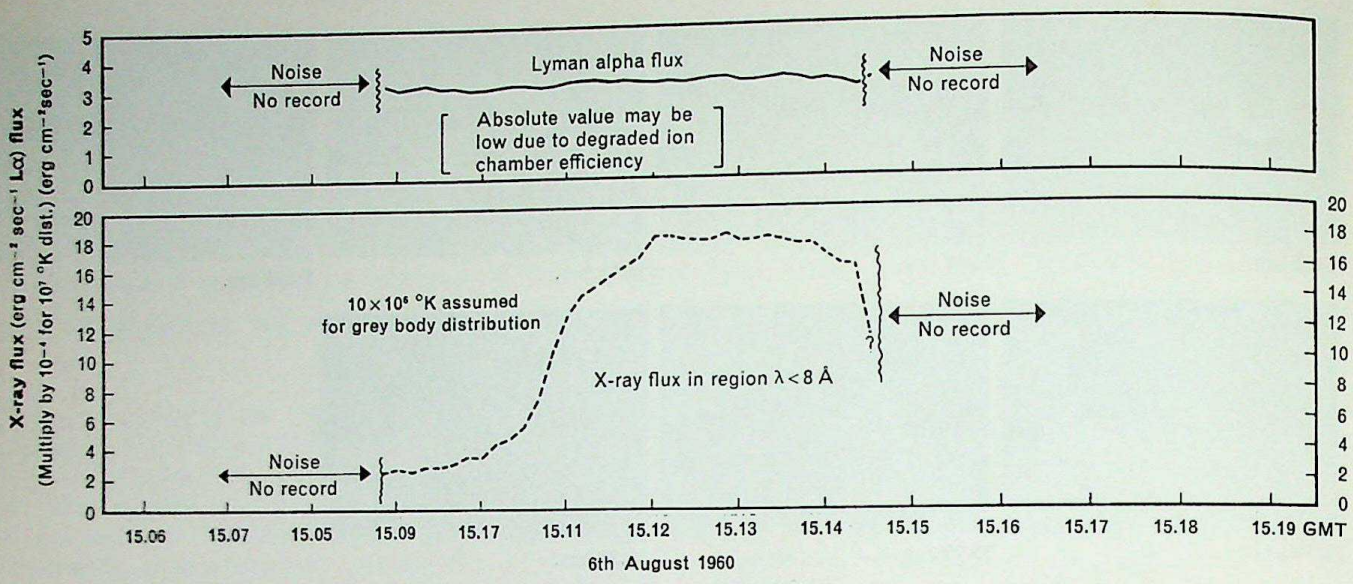

Figure 2 Rise in X-ray emission accompanying the flare shown in figure 1. Data recorded from a small satellite shows a rapid fivefold X-ray increase, while ultraviolet emission (Lyman alpha) from the Sun remains almost constant. A short-wave radio fade-out accompanied the flare.

position established for the main X-ray source. The real situation appears even stranger than was first concluded. The main source of non-solar X-rays striking the Earth is not the centre of the galaxy, but instead is what is referred to as an X-ray star, located in the constellation Scorpio [17]. The star is called Sco XR-1, and the astronomical co-ordinates are 16 hr 15 min Right Ascension, −15·2 deg. Declination. The accuracy of these measurements is believed to be about one degree. The amazing fact is that there is no peculiar radio or visible object at the position of Sco XR-1, yet it delivers to Earth a flux of X-rays, with a wavelength less than 8 Å, of 5×10^{-7} erg cm^{-2} sec^{-1}. Such a flux is equivalent in energy to the visible-light emission of a third-magnitude star.

All of the celestial sphere, except a small region near the south pole, has now been examined for X-ray stars. This series of studies has produced a list of about fifteen X-ray stars, the majority in the region of the galactic centre [18], but none of them comparable in strength to Sco XR-1 [18, 19]. They have a most interesting distribution in space, all but the original one (Sco XR-1) being within 15 degrees of the plane of the galaxy, and only one being more than 90 degrees in longitude away from the galactic centre. This distribution in space is similar to that of the recorded novae, and is probably not far from that of stars in the galaxy.

There is a strong indication that there are at least two types of X-ray star, apart from the Sun. One of the X-ray stars, the one farthest from the galactic centre, has been positively identified with a well-known astronomical object, the Crab Nebula. This is the third strongest radio star, and is also visible with good astronomical telescopes as a most peculiar optical object. It marks the position of a spectacular supernova explosion recorded in 1054 A.D. Both its visible and radio emission are attributed to vast clouds of high-energy electrons trapped in a tangled magnetic field. Such electrons produce a polarized radiation, which is known as 'synchrotron emission' because it is also observed inside the synchrotron electron accelerator. It is now believed that the X-rays produced in this object are produced by the same process. The Crab Nebula X-rays in the 1–10 Å band have been measured by Geiger counters flown in rockets; and more recently G. W. Clark [20] and L. Peterson [21] have detected X-rays in the 0·1–0·5 Å range from the Crab Nebula at altitudes attainable by balloons. This very broad spectral range of emission is that to be expected from the synchrotron process. However, the computed lifetime of electrons sufficiently energetic to cause synchrotron X-ray emission at 0·5 Å is much less than the time that has elapsed since the 1054 A.D. explosion. The emission poses two problems—how are these high-energy electrons replaced, and in what form is the required energy stored?

The visible Crab Nebula is very small, but it has been possible to measure the size of the X-ray source occupying its centre [22]. This measurement was made possible by calculations of eclipse times by the Greenwich Observatory. Eclipse (or lunar occultation) times for major radio sources are distributed by the Greenwich Observatory to radio observatories around the world in order to locate radio sources accurately, and to learn something about the shape of such sources. The author's laboratory received the occultation times for the Crab Nebula source, and as the Crab Nebula had been shown to be an X-ray star [17], the possibility of flying an X-ray detector during the occultation was conceived. The idea was most timely, as a partially constructed rocket frame was available for adaptation to the experiment in time for the occultation, 7th July 1964, which would be the last for eleven years. Moreover, the development of the large-area Geiger counters required for the study was well advanced, and a key flight test with them was scheduled for June. Most important, the development of the inertially guided attitude control system needed to keep the collimated Geiger counters pointing at the Crab Nebula throughout the upper portion of the rocket flight was also sufficiently far advanced to make the attempt worth while. NASA kindly made one of their directional controls available for the test, and the Space-General Corporation programmed the device for flight. Thus with great good luck and wholehearted participation by staff of the White Sands Missile Range and many other

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people, the experiment was accomplished less than six months after it was conceived.

The results of the Crab Nebula occultation experiment are shown in figures 3 and 4. Figure 3 shows the position of the Moon's edge during the development of the occultation as seen from the moving rocket. Figure 4 shows the counting rate of the collimated X-ray counters during the upper portion of the rocket flight. To understand the counting rate history we must know the flight programme. During the period from 90 seconds to 160 seconds after launching, the attitude control system on the rocket was manœuvring it so as to orient the counters toward the Crab Nebula. This caused the counters to point directly at the Sun during the period between 135 seconds and 155 seconds after launching, and solar X-rays caused the counters to saturate. After 160 seconds, the counters had been pointed to a position some 22 degrees beyond the Sun, a position quite close to the Crab Nebula. Between 160 seconds and 390 seconds after the launching, the counters remained pointed in a fixed direction to an accuracy of about a quarter of a degree. The Geiger counts observed from time $t=160$ seconds to $t=180$ seconds are a summation of counts produced by X-rays from the Crab Nebula, X-rays from a diffuse, probably extragalactic, background, and cosmic rays. The gradual decay in counting rate that occurs between $t=180$ seconds and $t=300$ seconds is due to the cutting off of Crab Nebula X-rays by the edge of the Moon. The fact that the decline in the flux of X-rays is gradual means that the source of X-rays is an object much larger than a normal star. Its angular size is 1 minute of arc: this corresponds to a diameter of about one light-year at the distance of the Crab. A size measurement has recently been made of the Sco XR-1 source by H. Gursky, R. Giacconi, P. Gorenstein, J. Waters, M. Oda, H. Bradt, G. Garmire, and B. V. Sreekantan. This scientific team has established that Sco XR-1 is less than 20 arc sec in angular extent. Results are being published in the 'Astrophysical Journal'.

The existence of two different types of X-ray stars is suggested not only by the difference in visible and radio emission between the Crab Nebula and Sco XR-1, but also by the difference in spectral character of the emissions. That of Sco XR-1 has been studied by G. Chodil, R. C. Jopson, H. Mark, F. D. Seward, and D. C. Swift [23], using a proportional counter flown in a rocket. Sco XR-1 shows a much more limited spectral emission than that of the Crab Nebula. The spectrum is analogous to that expected from a

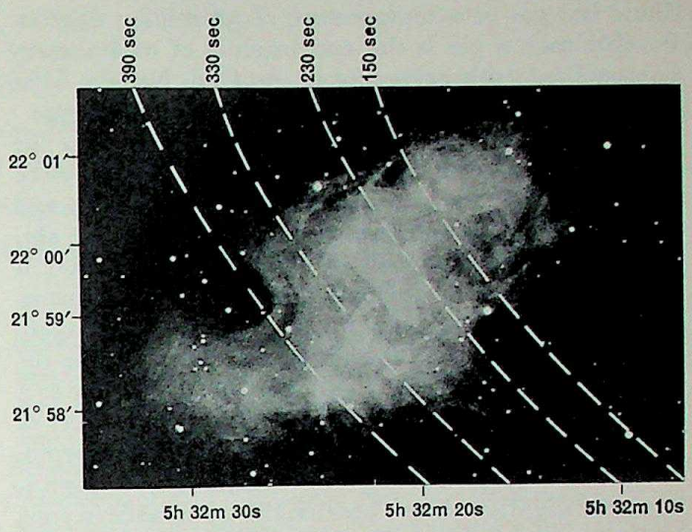

Figure 3 Calculated location of the edge of the Moon as seen from an Aerobee rocket at various times during a rocket flight designed to measure the size of the X-ray source at the centre of the Crab Nebula.

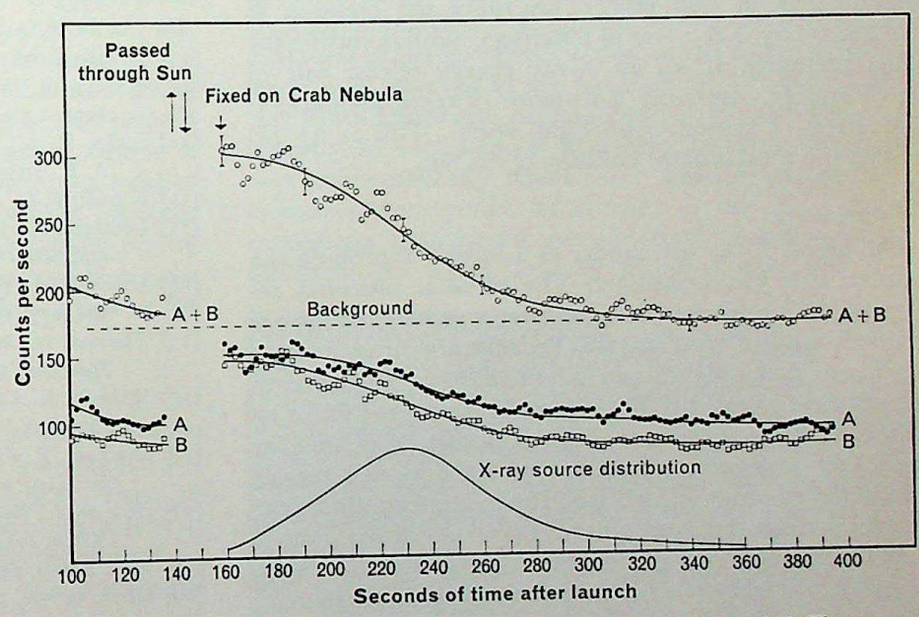

Figure 4 Counting rates observed by Geiger counters in an Aerobee rocket. The Geiger counters were kept pointing at the Crab Nebula during the period of lunar occultation.

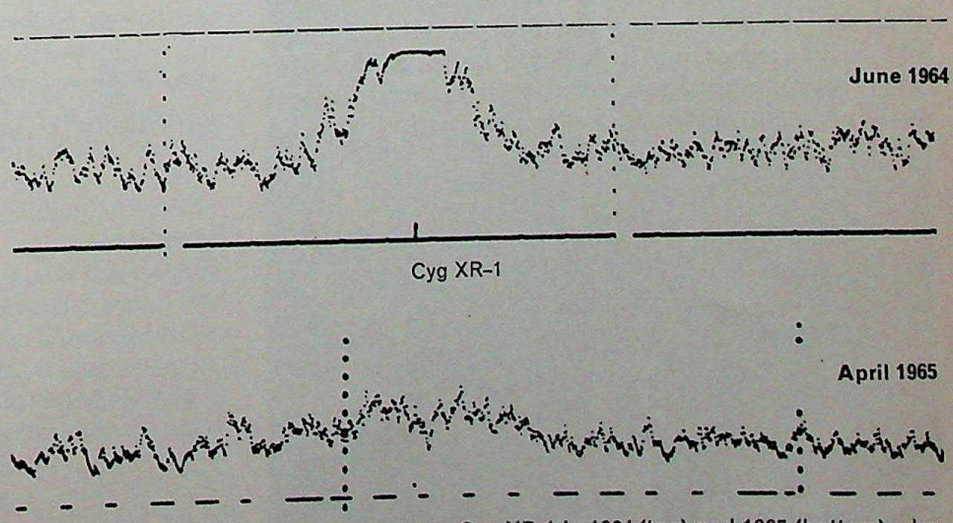

Figure 5 Signals produced by X-ray star Cyg XR-1 in 1964 (top) and 1965 (bottom) when collimated X-ray counters scanned across the source. The 1965 scans were slightly displaced from the source, which caused some reduction in signal strength; nevertheless, the data indicate a decrease in source emission by a factor of about four.

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dilute hot gas at a temperature of 58 million degrees. Possibly such a gas is the end product of evolutionary processes currently occurring in the Crab Nebula. Most of the X-ray stars appear to be of the Sco XR-1 type.

The X-ray star map is especially interesting in the constellation Cygnus. A sky scan study in 1964 showed clearly the presence of two main X-ray stars, XR-2 and Cyg XR-1, the second strongest X-ray star in the sky. The large signal recorded in 1964 from Cyg XR-1 is shown in the top half of figure 5. Almost identical instruments were used to map the sky in 1965, and again Cyg XR-1 and Cyg XR-2 were seen, but this time the radiation from Cyg XR-1 had dropped in intensity to a value equal to that of Cyg XR-2, while the intensity of the latter was the same as before. One of two responses observed in 1965 is shown in the bottom half of figure 5. They are slightly reduced because the scans made in 1965 were displaced from the Cyg XR-1 source by about three degrees; nevertheless, they are incompatible with the brightness measured in 1964. The 1965 scans indicate that Cyg XR-1 decreased in brightness by a factor of about four in one year. This raises the question of whether Cyg XR-1 was in a flaring condition during the first mapping. If so, an X-ray energy release rate of 10^{38} erg/sec (assuming a distance of three kiloparsecs) occurred (1 parsec = 3·26 light years). This is 2×10^4 times the total radiant emission of the Sun.

Future work

The use of X-ray astronomy as a means of probing the universe is just beginning. The celestial processes responsible for X-rays also produce emissions covering a broad band of wavelengths. Preliminary measurements indicate that only the emissions of shorter wavelength reach us from most of the sources. It seems probable that the longer wavelengths are being absorbed by interstellar gas. We can expect that more detailed work will permit an accurate study of this gas. It also appears that finer angular resolution and greater sensitivity will considerably increase the number of known X-ray stars. The 1965 sky scans already seem to indicate extragalactic sources. Weak sources have been found marking the locations of the strong extragalactic radio sources Cyg A and M87.

Even more exciting than the study of X-ray stars may be the analysis of the diffuse X-ray background. It seems probable, but not certain, that this background comes from outside our galaxy. R. J. Gould and G. R. Burbidge [24] believe that the background is due to the unresolved sum of many extragalactic sources. Alternatively it could be radiation arriving from the edge of the universe, that is, X-rays originating in an initial primordial explosion marking the start of the cosmic event. The wavelength of such X-rays would be lengthened by the red shift. If either hypothesis turns out to be correct, studies of the diffuse glow should provide valuable information for cosmological theory.

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Renaissance waterworks and hydromechanics

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A. G. Keller

Machines for moving water have a very long history—Heron of Alexandria devised small pneumatic and hydraulic toys during the first century A.D. However, the Renaissance saw a new interest in hydraulic machinery. Some of this was used for commercial purposes, but many of the devices were used for elaborate ornamental waterworks. Although these devices were mainly intended as amusements, the study of them played an important part in the downfall of Aristotelian physics.

Anyone who looks through the mechanical sketches of Leonardo da Vinci can hardly avoid being struck by the preponderance of instruments for raising water. His more famous designs, for flying-machines, or for mechanizing the production of tools and textiles, are greatly outnumbered by designs for pumps. The printed books of inventions that began to appear in the latter part of the sixteenth century tell the same story. In a society that in general showed little interest in technical progress, time and ingenuity were already being devoted to the invention and improvement of water pumps. Engineers did try to make improved cranes, mills, and engines of war, for example, but all the mechanical sketchbooks of the time seem to contain as many pumps as all other types of machine put together. In the largest of the early printed books on the subject, Agostino Ramelli's *Diverse et Artificiose Machine* of 1588, 116 plates, out of a total of 195, depict waterworks; they show machines for wells and foundations, and for drainage and irrigation (figure 1). It is clear that most of those who hoped to better the technology they saw about them were drawn first to this theme.

The inheritance from antiquity

For the most part, these Renaissance mechanicians sought only to refine the equipment they had inherited—antiquity had bequeathed them four basic types of hydraulic device. The simplest of these was the 'wheel of pots', an arrangement of pots lashed to the rim of an ordinary large wheel. Crude as it was, this instrument embodied the basic concept of continual transmission of power that marks the passage from tool to machine. The next development cannot have been too difficult: where the water supply was too far from the level to which it was to be raised for a single wheel to reach it, two wheels were used, one fixed at water level, the other above. An endless chain of pots linked them, the upper wheel driving the lower. Thus another essential feature was introduced—the linkage that ensures that remote parts can be driven by those more easily attainable. Later, the pots along the rim of the wheel were modified, becoming boxes hugging the curve of the wheel, or segments within it. The last arrangement permitted much more water to be raised, but it was not lifted so high; the water was poured out of a hole at the apex of the segment into a trough laid along the axle of the wheel. Where a waterwheel was used to draw water from a flowing stream and the current was strong enough, projecting blades were inserted, so that the river itself could turn the wheel. All these basic types are still to be seen in many villages of Asia and North Africa, and the engineers of the Renaissance knew of them from the craft traditions of their millwrights, as well as from the writings of the ancient Roman architect Vitruvius, their principal reference on machine construction. Two other types of water machine developed in antiquity attracted study in the sixteenth century. This was because of their supposed association with two of the heroes of ancient science. Vitruvius calls the force-pump 'the machine of Ctesibius', and it was commonly known by that name to the more scholarly engineers of the Renaissance, just as the name of Archimedes was attached to the water-screw. It was believed that force-pumps and Archimedean screws, having been invented by such famous men, must be more ingenious and mathematically based than other types. But the engineers were ready, of course, to use the simpler models too. Thus there is only one record of an engine that Leonardo da Vinci actually installed, and that is a

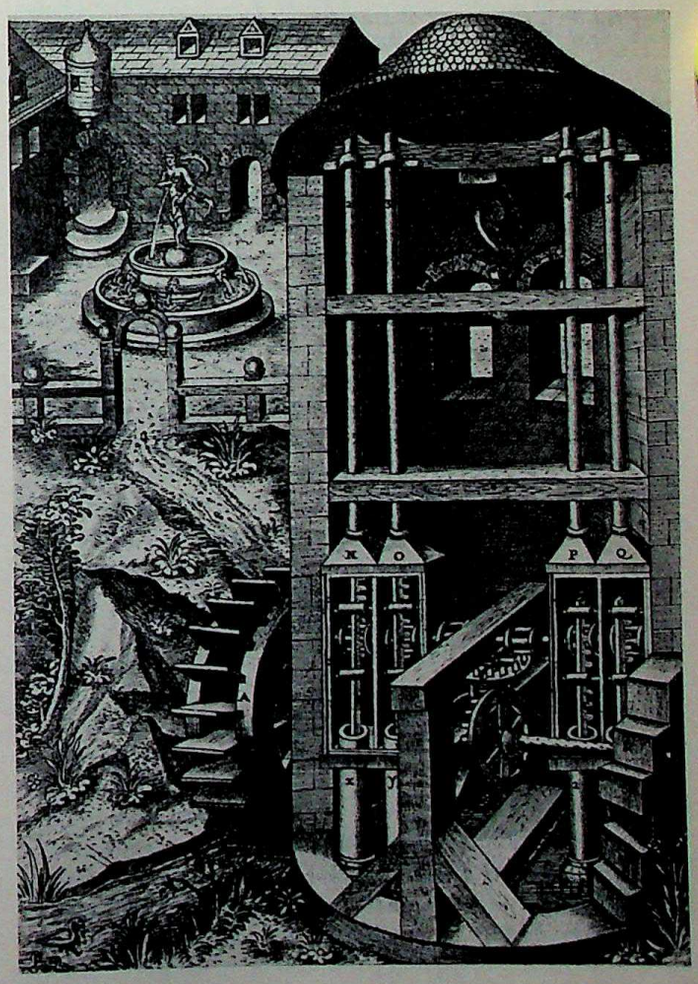

Figure 1 A pump designed to supply a fountain, operated by water power. (From Ramelli.)

A. G. Keller, M.A., B. Litt.
Was born in London in 1932, and educated at the Universities of Cambridge and Oxford. In 1960, he became assistant curator of the Whipple Science Museum of Cambridge University, and since 1963 he has been Lecturer in the History of Science at Leicester University. His particular research interest is the literature of mechanical inventions in the Renaissance.

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hand-operated waterwheel that differed not at all from its ancient prototypes.

Renaissance inventions

During the Renaissance, ingenuity was applied to devising elaborate systems for transmitting motive power rather than to devising new methods of drawing water in. But the early Renaissance has two important innovations to its credit—the rag-and-chain pump and the suction-pump. Those both appear for the first time in the sketch-book compiled about 1430–40 by the engineer Mariano di Jacopo. However, as he was nicknamed Taccola (the jackdaw) by his fellow-citizens, we need not assume that he invented either of the machines. The rag-and-chain pump must have developed from the chain of pots. Leather balls, stuffed with rags, were drawn up a pipe in an endless chain. The balls would be much lighter than the earthenware pots or wooden tubs used in the older machine, and loss through spilling could be virtually eliminated. As each ball rode up the pipe, the water below was forced into the pipe by the pressure of the water and the atmosphere above. The next ball would then lift the water up the pipe, for the balls would have swollen enough to provide a fairly tight seal.

The suction-pump, a modification of the force-pump, employed the force of atmospheric pressure more obviously. In the force-pump, water entered the cylinder because of the pressure of the water around it, and was then forced up an adjacent pipe by the piston as it descended: the suction-pump and its cylinder could be well above the surface of the water, and would receive its supply of water by atmospheric pressure as the piston rose. On the downstroke, a valve in the piston-head opened to admit water behind it, and as the piston rose again, it hauled the water up, almost like a bucket—it is sometimes known as a 'bucket-pump'. In one ingenious pump, erected at Fideris in Switzerland about 1550, the piston-head was constructed like an umbrella: it folded back on the downstroke and opened out again on the upstroke, so that the water would be hauled up behind it. The action of these suction-pumps created an intellectual problem—why did the water rise under the ascending piston-head, apparently against its nature? There could only be one answer in Aristotelian physics: a vacuum was a contradiction in terms, and could not exist in nature.

A third new pump—the rotary pump—was suggested at least, in the late Renaissance, again in the drawings of Agostino Ramelli. He shows us a number of designs in which drums, set eccentrically in a circular housing and equipped with vanes, impel water up an outlet pipe as they revolve. There is no evidence that these projects were ever constructed, but they show the interest of the best engineers of the period in developing completely new mechanical ideas.

Commercial applications

What was the reason for this absorbing interest in hydraulic machinery? The first motives to come to mind are economic ones, and there was certainly no lack of these. Marsh drainage and piecemeal reclamation had been attempted all through the Middle Ages, and ditches were cut across boggy land to drain it by gravitational flow; and by the sixteenth century it was becoming common for the sump that received the drainage to be emptied artificially, by pumping its contents into a prepared channel. Wind-powered water-wheels were already a feature of the Dutch landscape, and were first brought into England in the second half of Queen Elizabeth's reign. The French writer Montaigne, travelling through Italy in 1581–82, remarked on the many drainage schemes he passed on his road, several of which could be maintained only by the constant operation of pumps that delivered the water from trenches into a conduit.

In the north of Italy, irrigation was as important as drainage. This was possibly the consequence of changes in the agricultural pattern of the Po basin. Rice was introduced into the region about 1480. Giuseppe Ceredi published in 1567 a little book entitled *Il Modo d'Alzar le Acque de Luoghi Bassi* ('The method of raising water from low places'), which is our chief source of information on the diffusion of new inventions in hydraulic machinery at this time. He explains that many had flooded their lands to grow rice on them, and implies that it was possible to grow rich by so doing. Contemporary advocates of agricultural improvement bear him out in this. But Ceredi expresses a fear that keeping lands permanently under water would lead to 'putrefaction of the air', and so cause malaria. Profit and public health could be more easily combined by the temporary watering of meadows, using them afterwards as pasture again. Fra Leandro Alberti's *Descrittione d'Italia*, a guide-book printed in 1550, praises the fertility of the land thus irrigated. Near Lodi, for example, four or five crops of hay could be cut in a year, and 'so much milk is taken from the cattle to make cheese, that they make such cheeses as might seem almost incredible to those who have not seen them'. But even here Ceredi records the objection that more land given over to dairy produce meant less arable land—more beef and cheese for the rich, less bread for the poor. Nevertheless, most Italian states encouraged drainage and irrigation, and the Republic of Venice, the richest and always the most progressive, set up a commission for the '*Beni Inculti*' (the uncultivated lands) in 1561. This body was the first permanent authority for agricultural development. So many ideas for inventions were put forward, mainly for pumps, that the Venetian government started a collection of models to check new projects against existing patents.

Since the populations of many cities were growing, their ruling councils were keen to obtain fresh sources of water—wells, and the old conduits supplied by the flow from nearby springs, were proving increasingly inadequate. So the chronicles of European towns note the construction in the sixteenth century of new leats—open watercourses—and aqueducts. If there was no source at a higher level, water would be pumped up mechanically. The water-tower of Augsburg was celebrated for the height to which it raised water for distribution to the fountains of the city: the water was raised by a tower of Archimedean screws, each one supplying the one above, and all driven by pinions on a single axletree. A German engineer aroused great excitement when he erected the first water-powered force-pump at London bridge in 1582, especially when he was able to justify his boast to send a jet of water above the steeple of St Magnus. Montaigne noticed several pump-houses on his travels, with pumps arranged in two or even three storeys, because one alone could not lift the water to the desired height.

Water was also diverted to supply power for industry.

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Alberti mentions a sluice on the river Reno, near Bologna, which released water into a deep channel 'to turn various machines . . . to grind corn, to make copper vessels, and weapons of war, to pound herbs, and oak-galls (for dyeing), to spin silk, polish arms, sharpen various instruments, saw planks, make paper, with other services, and finally carry boats to Malalbergo'. But in general, diversions were made only where the water was available at the right level. It would seldom be economical to bring it any distance, and to pump it up in order to drive an engine was hardly practical. However, Ceredi does mention mills, at Venice and Ancona, that were operated by water that had first to be raised by horse-power, inefficient as it seems.

All these alterations to the original hydrography had their side-effects on the terrain. The Po basin had always been subject to floods, and conditions now worsened. Alberti suggested that deforestation and cultivation of the lower slopes of the Apennines was at the root of the trouble, for the hillsides were thus deprived of their protective cover, and rainwater ran off the slopes immediately. In addition, the newly reclaimed lands were precariously held; an excess of water might easily flood them again, or the channels that drained them might overload the rivers, so that they flooded somewhere else downstream. Further changes in the system sometimes caused even worse damage. An unsuccessful attempt to divert the Reno from flowing into the Po, ordered by the duke of Ferrara in 1542 had disastrous results. All the marsh land that had been recovered was drowned all over again, and navigation on the lower Po suffered, to the great ruin of the duke's own capital. As a result of these problems, an empirical science was developed to calculate the flow of water, and its effects. It is now becoming clear that the basic laws governing the flow of liquids were understood by the engineers of the sixteenth century, although we usually ascribe them to the work of Galileo's pupils, Castelli (*fl.* 1605) and Torricelli (1608–1647). They were certainly the first to derive these principles axiomatically from generalizations about bodies in motion, and erect them into a coherent science, but the fundamental concepts of hydrodynamics had already been perceived. Thus, the Renaissance '*conduttori d'acque*', as they were called, formulated proportions relating the quantity of water delivered, and the velocity at a given point, to the section and inclination of the river-bed. Nor was it just a matter of qualitative rules of thumb. In a recently discovered manuscript written about 1560 by Juanelo Turriano, an Italian engineer in the Spanish service, we find a geometrical and quantitative treatment of the flow of water over a weir or past an obstacle in the stream, and calculations as to the amount delivered by a given orifice under a given head. In addition to these elementary studies in hydrodynamics, Turriano analysed geometrically the ideal shape for waterwheel blades, and the correct angle for the jet to strike them (figure 2).

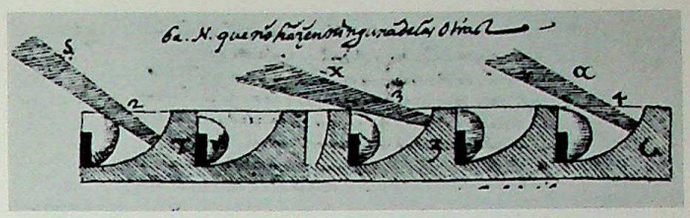

Figure 2 Turriano's theoretical analysis of the design of a waterwheel blade.

Waterworks in architecture

But practical utility was not the only reason why pumps attracted the interest of the learned. More enthusiasm seems to have been generated at the time by the exploitation of waterworks for entertainment. To the men of the Renaissance, water was not merely a necessity for drinking and for irrigating their fields and kitchen-gardens—it could also be a delight to the eyes. So the palaces of kings and nobles were graced with fountains in every courtyard, and cities erected them in their squares. What had presumably begun as an imitation of the ancient Roman style, which had made some use of artificial springs and pools of water, now became a principal feature of architectural ornament. To be complete, a garden must have its fountain-jets, to cool the air and set off the static mass of the building by their fluid mobility. The jets would require a considerable quantity of water, which would have to be supplied with a head sufficient to raise them to a fitting height. But this could not always be provided by nature. Moreover, the really thorough-going water-garden enthusiast would not be content with simple jets. Fifteen centuries before, in the first century A.D., Heron of Alexandria had described some seventy 'pneumatic' devices, little mechanical toys for the most part, which worked by the pressure of air or water. Inspired by Heron, the fountain builders of the Renaissance designed their own ingenious automata, which attracted even more admiration than the fountains (figure 3). When visiting royal mansions and country villas, the traveller looked first at the water-powered mechanical statues; listened to the hydraulic organs (figure 4); and might be drenched by sprays operated by concealed springs or levers, to the great diversion of all who stood at a safe distance (figure 5). Montaigne weighed up the comparative merits of the most celebrated water-gardens of Italy—Pratolino outside Florence, and the Villa d'Este at Tivoli: 'In diversity of the entertainments and pleasant movements driven by the water, they are equal, unless it be that the Florentine has somewhat more delicacy in the disposition and order of the whole ensemble, the Villa d'Este in antique statues and palaces'. Many fine drawings and plates of these pneumatic devices have survived, particularly from the turn of the seventeenth century, when the vogue was at its height. When G. B. Aleotti, an engineer employed by the duke of Ferrara, published the first Italian translation of Heron's *Pneumatica* in 1589, he appended four new automata of his own invention, and in a second appendix described a four-cylinder force-pump, which could supply water to his automata, and gave full directions for its construction and maintenance. Four alternative systems of transmission were proposed, for driving the pump by man, horse or waterwheel. Some years later, he added, in manuscript, drawings and descriptions of other automata planned or installed, and other pumps, so that we can know exactly what some of these devices looked like, and how they worked.

Whereas Heron had been thinking usually in terms of small-scale models, to be set up on a table, or at least indoors, it is apparent that Aleotti and his fellows intended something much bigger. In fact here, as in so many spheres, the Renaissance significantly altered its inheritance from antiquity, by moving its pneumatic

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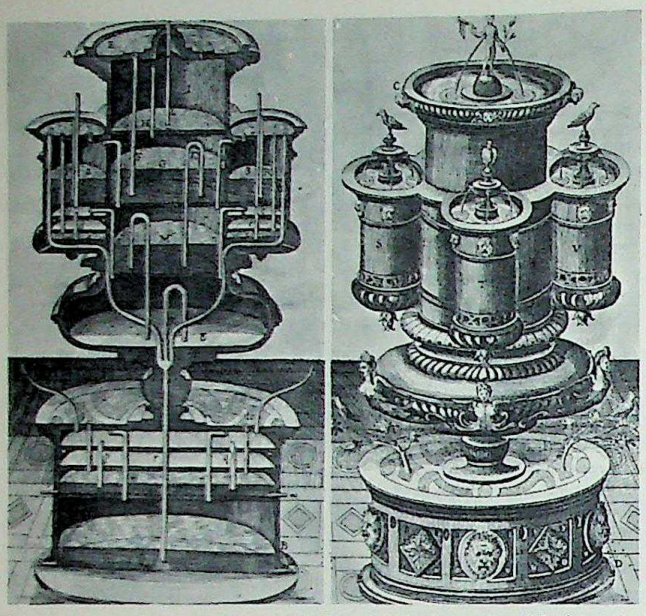

Figure 3 A 'Heron's Fountain'. The bird automata whistle and wag their tails. (From Ramelli.)

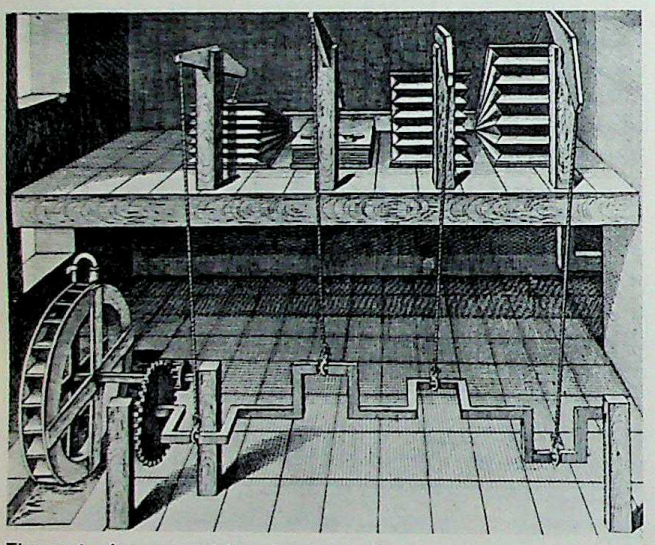

Figure 4 An organ driven by water. (From S. de Caus, 'Les raisons des forces mouvantes'.)

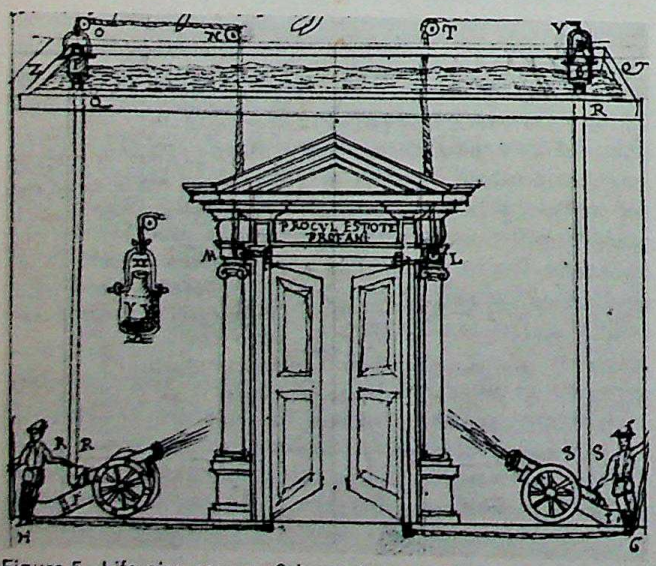

Figure 5 Life-size cannon-firing automata. The cannon squirted water on anyone who opened the door. (From a manuscript by G. B. Aleotti, *c.* 1610.)

amusements out of doors and making them much larger. In addition, the water-garden was meant to instruct as well as to entertain. Pneumatic devices were in a sense laboratory apparatus, except that they were designed to demonstrate known facts about nature, rather than find out new ones, and Heron himself had prefaced his book with a discussion on the vacuum. Although he had concluded that an artificial vacuum might be possible, and that there were micro-vacua in the interstices of solid matter, almost all his Renaissance followers accepted the Aristotelian orthodoxy, that no vacuum could exist under any conditions. Aleotti used Heron's language, but he came down firmly on the conventional side. It is true that at times he seems to admit some of Heron's doctrines almost without thinking, but consciously he asserts the opposite, and even believed he could put forward fresh reasons against the possibility of a vacuum, taken from everyday experience. This indeed was the general consensus.

The existence of the vacuum

If these pneumatic automata were supposed to display certain natural phenomena, what happened if they failed to perform? Here the significance of repeating the experiments on a larger scale is made plain to us. If, like Heron, the student of pneumatics attached his siphon to a table-jug, all went well, for the pressure of the atmosphere could lift water over the crook of the siphon into the further leg. The experimenter could suppose that he had demonstrated the power of nature's horror of the vacuum, and even extrapolate unwisely to declare that horror absolute. But what would happen if a giant siphon were constructed to lift water over a ridge? A young disciple of Galileo, called Baliani, observed that his large siphon did not work at all as he had expected, and wrote to Galileo about it, offering an explanation which came much closer to the truth than that of his mentor. Galileo himself still held to the concept of a natural resistance to the vacuum, although he observed that this resistance was limited; and he suggested both a reason for the limit, and a way of measuring it. It is well known that he adduced as his prime argument the inability of suction-pumps to raise water above 32 feet. As the suction-pump was comparatively novel, and had been generally diffused only in the past hundred years or so, this fact had presumably not long been realised, but by the end of the sixteenth century, writers on engineering often distinguish the force-pump by its capacity to raise water 'to the top of any high tower', or 'to an inordinate height'—even to the very stars, if you but had a pipe strong enough. Once the limitation of the suction-pump had been recognized, Galileo's searching mind would try to explain it, and link it to other anomalies in the traditional system, such as the parallel limitation of the siphon. While it would seem unlikely that he was first drawn to the problem of the vacuum by this information from common experience, he was always looking for such evidence to use in his assault on the old scholastic physics.

Undoubtedly, the popularity of these hydraulic devices familiarized a wide public with the basic theories of pneumatics, and created a general interest in the problems they gave rise to. This was the age of the scientific amateur, and such men would be most eager to discuss a problem whose manifestations they could scarcely avoid noticing. The very instruments used to

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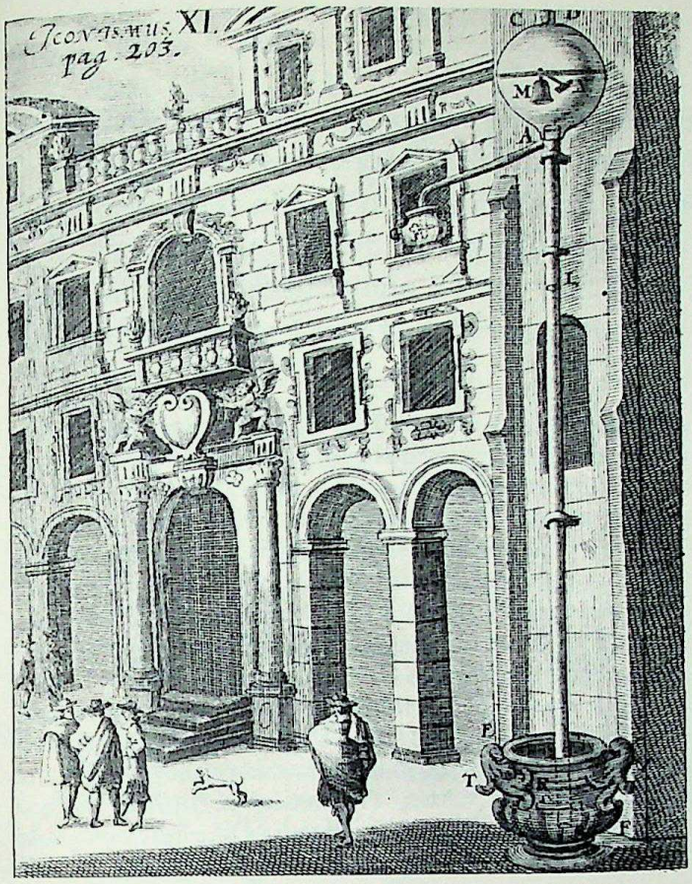

Figure 6 The experiment by G. Berti to demonstrate that a vacuum could exist. (From C. De Waard, 'L'expérience barométrique'.)

subvert the old science and establish the new were also built up from these devices. Practical force-pumps suggested models for the apparatus which Blaise Pascal designed in the 1640s for his experiments on the hydrostatic paradox. Indeed, Leonardo da Vinci, and other mechanicians later in the sixteenth century, had already been playing with the ideas involved, which could have followed easily enough from attempts to express the force exerted by the piston in quantified terms, as a function of its weight, section, or the power of its motor. But Leonardo's sketches were mostly brilliant ideas, thrown off and then abandoned, while Pascal integrated these concepts with the new developments in a systematic mechanics. But, as we can see from the illustrations to his treatise, the actual machinery is the same.

As much might be said of the apparatus used in the crucial experiments on the vacuum. Galileo's proposed method for testing the strength of the resistance to a vacuum employed the piston and cylinder of the suction-pump. Indeed, it was no more than an upturned pump with a weight at the end of the piston. This weight could be increased until the piston began to move down the cylinder, leaving a vacuum above it, so as to give the experimenter a quantitative limit to the *horror vacui*. The early air-pumps of Guericke and Boyle, constructed in the decade after Pascal, used the same traditional components. But the instrument designed for the first successful experiment on the vacuum, instigated, or at least inspired, by Galileo, depended even more on inherited techniques. About the year 1640, a certain G. Berti, otherwise almost unknown, set up an instrument which seems to have been taken straight from one of those books of pneumatic entertainments after the style of Heron (figure 6). We can see an exact parallel with the kind of very elaborate siphon drawn by Aleotti or Della Porta—the same pipe with the same stopcock at the bottom to drain the same glass bowls. However, Berti's approach was the opposite to that of his predecessors. Had they been right, the water in his pipe would never have fallen. Indeed, Della Porta had supposed that the water could be raised from another lower bowl, whatever their relative volumes and distances, rather than allow a vacuum to be formed. As, however, the water did fall in Berti's pipe, he concluded that he had demonstrated the existence of a vacuum beyond all doubt.

Pure theoretical research very often repays its borrowings from the technical realm at a later stage, and one may reflect that the same happened in this case. There is no need to point out that Pascal's hydrostatic thesis led, ultimately, to the hydraulic press, or that the steam-engine could never have been invented without the studies on the vacuum. Indeed, the first suggestions of the mechanical possibilities inherent in the expansive power of steam also occur in the literature of water-garden automata. Salomon de Caus made the first explicit statement in 1615 in his book *Les raisons des forces mouvantes*, in which he describes a little fountain for raising water by steam pressure, in the course of a theoretical preface to the book. Most of the plates in this book are of dumb-shows of scenes from classical mythology, together with hydraulic organs to provide musical accompaniment, and pumps to supply the water. As De Caus was a well-known designer of gardens and grottoes, and had laid out water-gardens for the Prince of Wales, and the Elector Palatine at Heidelberg, it is only to be expected that he would see this invention as another potential showpiece, combining intellectual stimulus with aesthetic pleasure. The search for new entertainment and delight, no less than economic developments, provided a suitable atmosphere for experiment and discovery. At first advances were confined to the immediate field of fluid mechanics, but the repercussions affected almost every aspect of the new physics then struggling to be born.

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Polyhedral boranes, carboranes, and carbametallic boron hydride derivatives

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M. F. Hawthorne

The atoms in some forms of elementary boron are arranged in polyhedra, and a number of new types of boron hydride derivative, based on this structure, have been discovered in recent years. These include new polyhedral ionic species, carboranes, in which certain sites in the boron polyhedron are occupied by carbon atoms, and new carbametallic boron hydride derivatives. This article describes the preparation and reactions of these new species and structural and bonding problems that arise. It also draws attention to the aromatic character of many of the compounds.

The ability of boron to bond with itself and form a series of hydrides was first recognized by Alfred Stock [1] in the early 1900s. Examples of these classical boron hydrides are the compounds B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ (figure 1). Decaborane-14 ($B_{10}H_{14}$) is the only member of this group that can be handled in air without spontaneous ignition or hydrolysis, or both. In fact, the high reactivities displayed by the first known boron hydrides, coupled with their relative scarcity and the need to work with small quantities, led Stock to develop special high-vacuum techniques for their manipulation. These have played an important part in the subsequent development of the field.

It is hardly surprising in these circumstances that the first known boron hydrides were considered to be mere chemical curiosities. They presented unusual valency problems, for their formulation in terms of normal two-electron bonds proved impossible, and this 'electron deficiency' provided a basis for the later study of multicentre bonding. The solution of the bonding scheme in B_2H_6 by W. C. Price [2] was rapidly followed by detailed X-ray diffraction studies of the higher members of the borane series. This work was coupled with the development of appropriate bonding descriptions based on both the valence-bond method and the LCAO (linear combination of atomic orbitals) method. The greater part of these structural and bonding problems were resolved by W. N. Lipscomb and his associates [3] during the last fifteen years. Until very recently, most of the boron hydrides were characterized by structures that could be recognized as fragments of the icosahedron (a regular structure with 12 apices and 20 faces) or the octahedron.

Boron atoms tend to cluster so as to form fragments of icosahedra, and the atoms in certain forms of elemental boron are arranged in actual icosahedra. These facts led H. C. Longuet-Higgins and M. de V. Roberts [4] to investigate theoretically the then hypothetical icosahedral $(BH)_{12}$ borane. They used the molecular-orbital method, and, as a result of this work, the $(BH)_{12}$ system was predicted to attain maximum stability and a filled orbital configuration when two 'extra' electrons were added to the system. The icosahedral $B_{12}H_{12}^{-2}$ ion was thus predicted four years before its first description in the chemical literature [5]. The $B_{12}H_{12}^{-2}$ ion has a high degree of symmetry, and requires more than 70 contributing structures for a complete description in terms of valence bonds. This suggests that the electrons involved in polyhedral bonding are extensively delocalized. It is therefore tempting to assume that the $B_{12}H_{12}^{-2}$ ion and other polyhedral boranes of high symmetry have considerable resonance energy, and that such species are aromatic members of the boron hydride family.

Three classes of polyhedral borane are known, and this article will consider all three classes. The first is exemplified by $B_{12}H_{12}^{-2}$, and comprises a series of polyhedral $B_nH_n^{-2}$ ions. Theoretical arguments suggest that there may be ions with all values of n between 5 and 12, inclusive: ions with $n=12$, 11, 10, 9, and 6 have already been prepared.

The species of the second class are electrically neutral and are formally derived from the $B_nH_n^{-2}$ ions by replacing two boron atoms by two electronically equivalent C^+ ions. If these hypothetical substitutions are studied theoretically, it is found that the series $B_{n-2}C_2H_n$ should exist, and should be isoelectronic with the corresponding $B_nH_n^{-2}$ ions. The two carbon atoms can be in different positions relative to one another, resulting in isomers. Compounds of this type have been recognized for several years and have been called 'carboranes'. At least one isomer of each carborane system has been described with values of n from 5 to 12, and all possible isomers are now known in several carborane systems.

The third class of polyhedral species results from replacing a boron atom in an icosahedral $B_{10}C_2H_{12}$ carborane with an element other than boron or carbon. These replacement reactions have been accomplished with a number of transition-metal ions [6], including iron, cobalt, manganese, and rhenium. The resulting complexes are closely analogous to the well known cyclopentadienyl metallocenes, and therefore display aromatic properties. Compounds of this type are described as 'carbametallic boron hydride derivatives' or 'metallocarboranes', and link transition-metal chemistry with that of the boron hydrides.

Reference has been made already to the concept of polyhedral aromaticity in relation to the $B_{12}H_{12}^{-2}$ ion and to other polyhedral boranes of high symmetry. This is associated with the delocalization of electrons involved in polyhedral bonding and is supported by the synthesis of a large number of polyhedral borane systems, combined with detailed structural information and bonding descriptions. In addition, the inherent stability of the known polyhedral boranes and the nature of their characteristic reactions bear a similarity to the corresponding properties of the aromatic hydrocarbons.

M. F. Hawthorne, *B.A., Ph.D.*

Born at Fort Scott, Kansas, in 1928, and educated at Pomona College and the University of California. After a period of research work at Iowa State College he became a Senior Research Chemist at the Redstone Arsenal Research Division of Rohm and Haas Company. He has been a Professor of Chemistry at the University of California since 1962. His research interests are in the synthesis and reactions of inorganic and organic compounds of boron.

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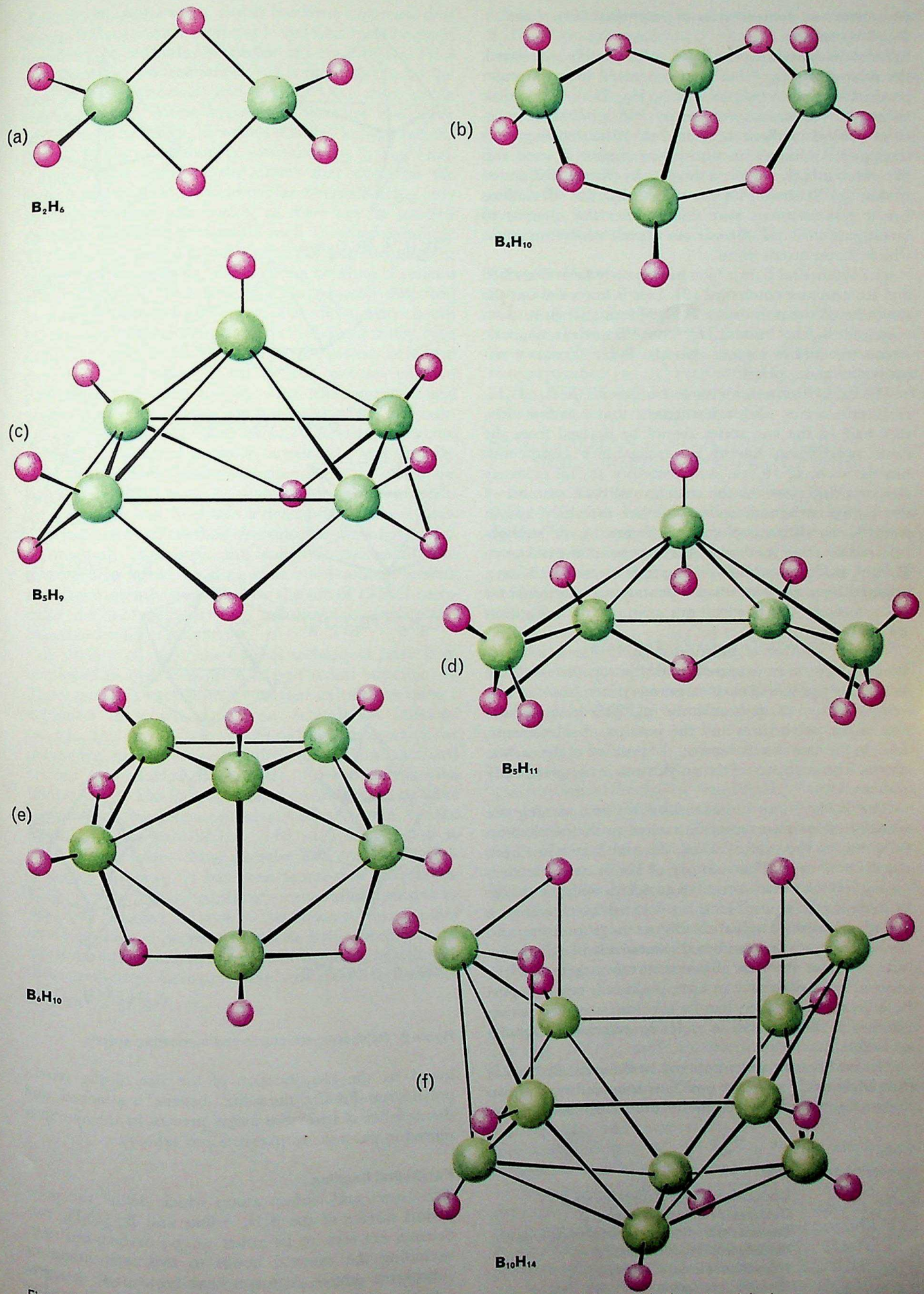

Figure 1 Representative boron hydrides with structures that resemble fragments of the icosahedron or octahedron.

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Structures and nomenclature of polyhedral $B_nH_n^{-2}$ and $B_{n-2}C_2H_n$ species

Before salts containing the $B_{12}H_{12}^{-2}$ ion had been isolated, the related $B_{10}H_{10}^{-2}$ ion was recognized [7] as a major product in certain reactions of $B_{10}H_{14}$. Both ^{11}B nuclear magnetic resonance spectroscopy and qualitative molecular orbital methods suggested that this ion formed a bicapped Archimedean anti-prism (figure 2), and this has subsequently been confirmed by X-ray diffraction studies [3]. It should be mentioned that the ^{11}B nucleus has a spin moment and this enables the chemist to investigate in detail the various atomic environments in which boron atoms occur.

The octahedral $B_6H_6^{-2}$ ion has recently been described and its structure confirmed [8]. Less is known about the structure of the only other $B_nH_n^{-2}$ ions that have been prepared, $B_{11}H_{11}^{-2}$ and $B_9H_9^{-2}$, but ^{11}B nuclear magnetic resonance studies suggest that the $B_9H_9^{-2}$ ion is a tricapped trigonal prism.

The $B_nH_n^{-2}$ ion series is isoelectronic with the $B_{n-2}C_2H_n$ carborane series, and this suggests that corresponding members of the two series should be derived from the same polyhedron having n vertices. For compounds having $n=6$, 9, 10, 12, and probably 11, all evidence supports this view. As the structure of each member of the entire carborane series is either definitely known from X-ray diffraction studies (figure 2), or strongly inferred by other methods, the structures of the unknown $B_5H_5^{-2}$, $B_7H_7^{-2}$, and $B_8H_8^{-2}$ ions may be predicted—as a trigonal bipyramid for $n=5$, a pentagonal bipyramid for $n=7$, and an Archimedean anti-prism or dodecahedron for $n=8$.

A large number of substituted $B_nH_n^{-2}$ ions and carboranes have been prepared, and this, together with the isomerism possible in each carborane system, has led to a unique system of nomenclature [9]. This identifies the size of the polyhedron and the position of substituents, and, in the case of a carborane, the position of the carbon atoms. The geometry of the polyhedron is not specifically indicated.

The $B_nH_n^{-2}$ ions are identified by first naming the number of hydrogen atoms attached to the polyhedron followed by the prefix 'clovo', derived from the Greek word for a cage. The number of boron atoms is then given, and the suffix '-borate' is attached, with the charge in parentheses. Substituents are located by choosing an actual or imagined apical position as the '1' position, and the boron atoms are numbered successively in a clockwise fashion about the belt of boron atoms attached to the selected apex position. An apex position is one occupied by a framework atom having the lowest co-ordination number in the polyhedron under consideration (figure 2 and table 1).

The carboranes are numbered in the same fashion as the polyhedral ions. The positions occupied by the two carbon atoms are identified by numerical prefixes followed by the identification of the size of the parent polyhedron. Finally, the suffix '-borane' is attached, and the number of hydrogen atoms present in the system is placed in parentheses (figure 2 and table 1).

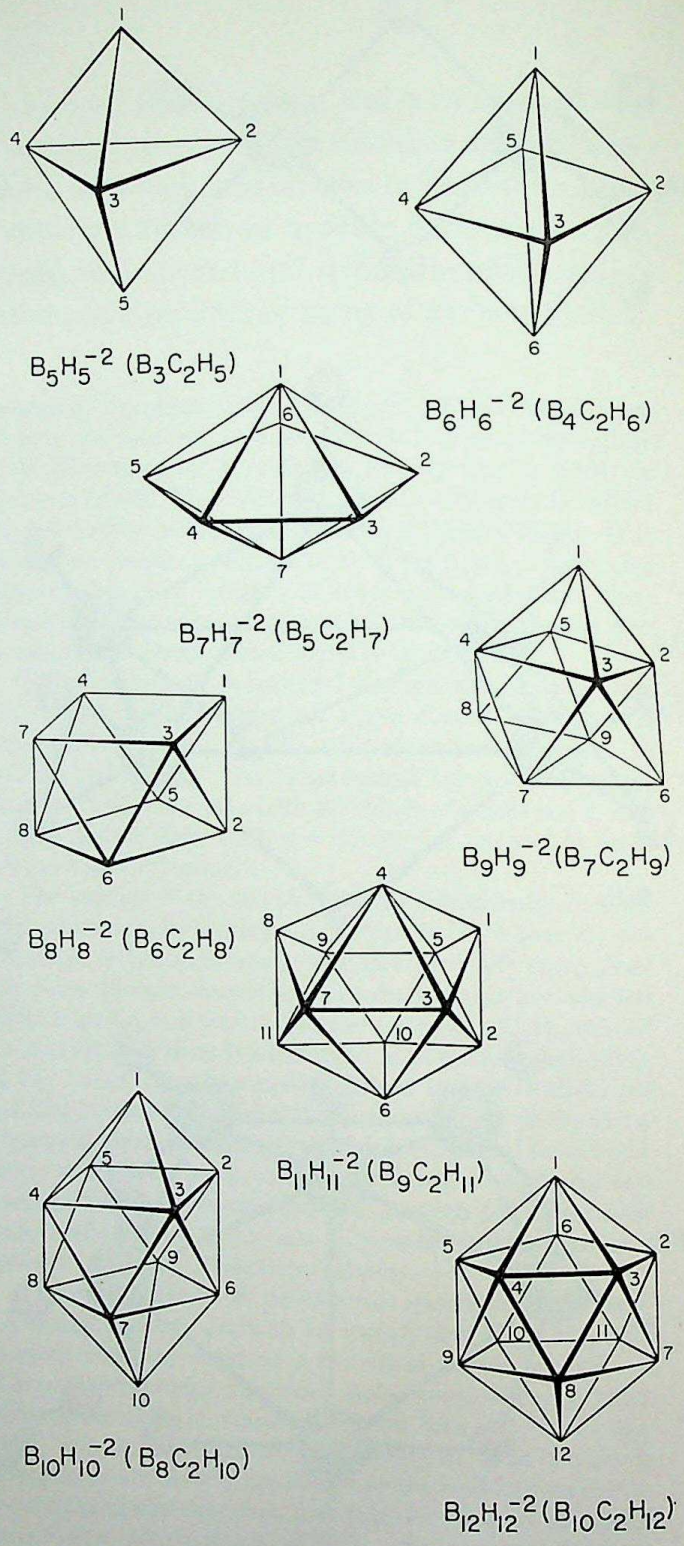

Figure 2 Polyhedral structures and numbering system.

Table 1
Nomenclature examples

$B_{12}H_{12}^{-2}$	Dodecahydroclovododecaborate (2−)
$B_{10}C_2H_{12}$	Dicarbaclovododecaborane (12)
$B_{10}C_2Cl_{12}$	Dodecachlorodicarbaclovododecaborane (0)
$B_{10}H_{10}^{-2}$	Decahydroclovodecaborate (2−)
$B_{10}Cl_{10}^{-2}$	Decachloroclovodecaborate (2−)
$B_8C_2H_{10}$	Dicarbaclovodecaborane (10)

Polyhedral bonding

The boron and carbon atoms which define the polyhedral surface of the $B_nH_n^{-2}$ ions and $B_{n-2}C_2H_n$ carboranes are seen to be either 4-, 5-, or 6-co-ordinate, excluding the external bonds to hydrogen atoms or substituent groups. Attempts have been made to correlate chemical reactivity with the co-ordination number

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of the atom in question, and it has been suggested that polyhedral species are most stable and least reactive when boron is 5-co-ordinate and carbon is 4-co-ordinate. Thus 1,10-dicarbaclovodecaborane(10) is predicted to be the most stable carborane, and $B_{12}H_{12}^{-2}$ the most stable polyhedral ion. These hypotheses have not been fully tested experimentally. However, it is well known that the $B_{10}H_{10}^{-2}$ ion is much more reactive than the $B_{12}H_{12}^{-2}$ ion.

Interactions between the atoms that comprise the frameworks of polyhedra cannot be described using only 2-centre electron pair bonds, as there are far too few electrons available to provide such localized bonding. The valence-bond method is generally not adequate for polyhedral compounds, although the bonding of systems of low symmetry, such as B_4H_{10}, is adequately described by a single structure comprised of 2- and 3-centre bonds [3]. Similarly, species of somewhat higher symmetry, such as B_5H_9, may be described in terms of a resonance hybrid composed of several distinct 2- and 3-centre electron pair bond structures which, when taken together and properly weighted, retain the symmetry of the molecule.

Even for such molecules, the LCAO molecular orbital method [3], referred to above, is valuable, and as molecular symmetry is further increased, as in the case of the larger polyhedral systems, many more canonical structures are required to obtain a description of the hybrid. The valence-bond method therefore becomes less useful. Throughout chemistry, the study of molecules that involve delocalized bonding over many atomic orbitals have been greatly simplified by the use of LCAO molecular orbital methods: the treatment is particularly valuable for large polyhedra.

A variety of molecular-orbital techniques have been employed in the description of polyhedral bonding [3]. These methods vary from a complete calculation using a computer in which all atomic orbitals are included ($2s$, $2p_x$, $2p_y$, and $2p_z$), to simplified methods in which the polyhedral structure is artificially separated into localized regions and each region treated in a different fashion (figure 3) [3]. The most simplified methods yield no more than the expected electron balance of the system, but the more complete calculations yield such information as relative molecular-orbital energies and charge distributions. In this way, it has been found that the carbon atoms present in polyhedral carborane surfaces tend to be positively charged, relative to the boron atoms. Another result of these detailed treatments is the prediction of electrophilic substitution reaction sequences, although these predictions have not so far been completely successful. As an example, the apical (1 and 10) positions of the $B_{10}H_{10}^{-2}$ ion are predicted by charge distribution calculations to be much more reactive in electrophilic substitution reactions than the equatorial positions, since the apical positions carry a partial negative charge. However, certain electrophilic reagents are actually inert toward the apex positions and readily react at the equatorial positions. The failure of the prediction is probably not a result of a faulty description of the $B_{10}H_{10}^{-2}$ ion, but rather the result of the simplifying assumption that the transition states of the substitution reactions always closely resemble the ground state $B_{10}H_{10}^{-2}$ ion.

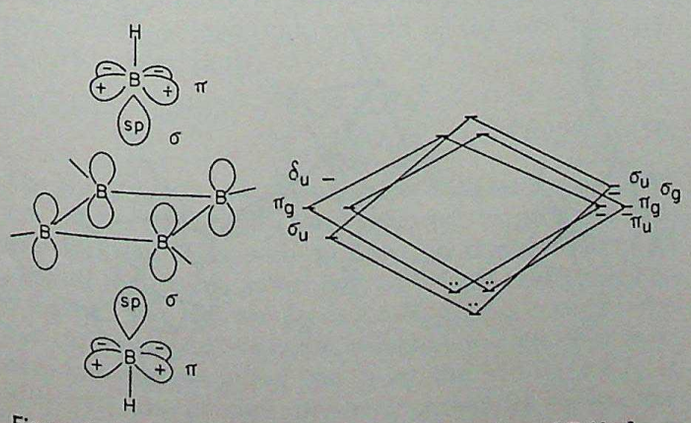

Figure 3 Simplified molecular orbital description of $B_6H_6^{-2}$, using arbitrarily selected apices.

Polyhedral ions

Preparation

Salts of the $B_{12}H_{12}^{-2}$ ion have been prepared by a variety of synthetic procedures which involve the building up of the icosahedron from smaller fragments. The most attractive preparation [10, 11] employs B_2H_6, and a Lewis base or the BH_4^- ion, and nearly quantitative yields are obtained at temperatures near 150°.

$$6B_2H_6 + 2(C_2H_5)_3N \rightarrow 2(C_2H_5)_3{}^+NH + B_{12}H_{12}^{-2} + 11H_2$$
$$5B_2H_6 + 2NaBH_4 \rightarrow 2Na^+ + B_{12}H_{12}^{-2} + 13H_2$$

By modification of this procedure, $B_{10}H_{10}^{-2}$ and $B_6H_6^{-2}$ [8] may be obtained. Salts of the $B_9H_9^{-2}$ and $B_{11}H_{11}^{-2}$ ions have also been prepared, but the methods used have not been published.

The reaction of $B_{10}H_{14}$ with an amine such as triethylamine [7] provides a convenient and quantitative route to $B_{10}H_{10}^{-2}$.

$$B_{10}H_{14} + 2(C_2H_5)_3N \rightarrow [(C_2H_5)_3{}^+NH]_2B_{10}H_{10}^{-2} + H_2$$

The mechanism of this reaction has been studied [12] and the available evidence indicates that $B_{10}H_{12}[N(C_2H_5)_3]_2$ and $B_{10}H_{12}N(C_2H_5)_3$ are intermediates in the overall reaction.

Reactions

The reactions of the $B_{12}H_{12}^{-2}$ and $B_{10}H_{10}^{-2}$ ions have been extensively investigated because they are readily available, and it has been found that they form an extensive range of derivatives that resemble those of the aromatic hydrocarbons. Both $B_{12}H_{12}^{-2}$ and $B_{10}H_{10}^{-2}$ are susceptible to apparent electrophilic substitution, and $B_{10}H_{10}^{-2}$ is readily oxidized to $B_{20}H_{18}^{-2}$ (figure 4) [13], and this, in turn, undergoes a series of interesting reactions which often involve intramolecular rearrangements [14].

Representative electrophilic reagents which readily attack either the $B_{12}H_{12}^{-2}$ ion or the $B_{10}H_{10}^{-2}$ ion, or both, without disrupting the polyhedral framework include the halogens (Br^+), acyl halides (RCO^+), oxalyl chloride (CO^+), and aryldiazonium ions ($\varphi N{\equiv}N$). These reactions often proceed most readily in strongly acidic reaction media. The precise mechanism of these substitution reactions is unknown. They appear to be electrophilic, but there seems to be more than one mechanism. In general, the $B_{10}H_{10}^{-2}$ ion is much more susceptible to substitution than is $B_{12}H_{12}^{-2}$. A clear case of this reactivity difference occurs in the reaction with the benzene diazonium ion [15]. In this case, $B_{12}H_{12}^{-2}$ reacts very slowly, if at all, but one apical position of the $B_{10}H_{10}^{-2}$ ion is substituted instantaneously. The resulting azo derivative is extremely basic and the $B_{10}H_9NH{=}N\varphi^-$ ion is the product isolated. The fact that the azo

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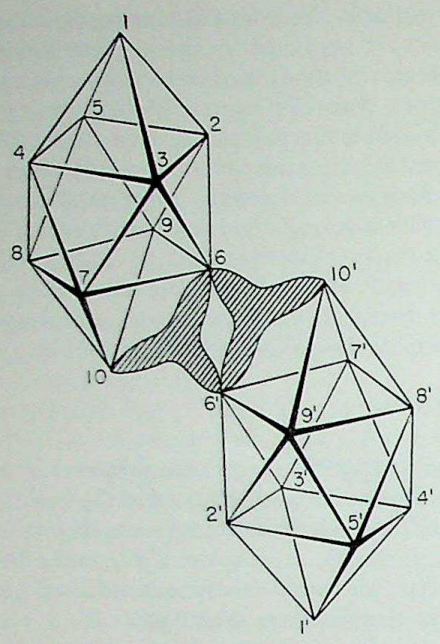
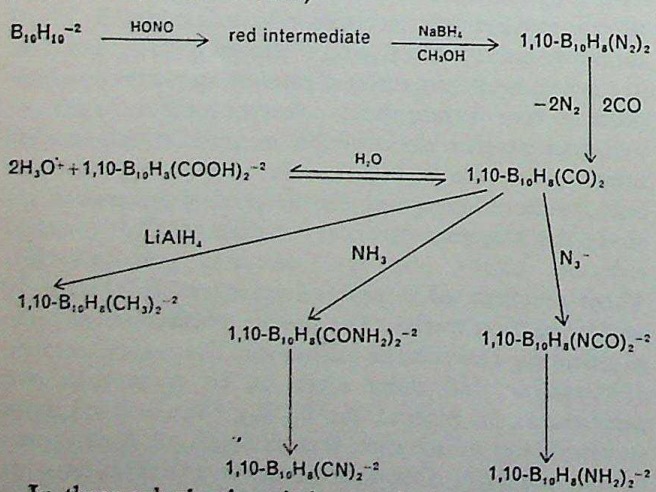


Figure 4 Structure of $B_{20}H_{18}^{-2}$ with hydrogen atoms removed.

derivatives are highly coloured and resemble the azo dyes derived from aromatic hydrocarbon systems agrees with the suggestion that the bonding electrons in the $B_{10}H_{10}^{-2}$ polyhedron are delocalized. The extreme basicity of non-bonded electron pairs associated with an atom which is directly attached to the $B_{10}H_{10}^{-2}$ polyhedron may be rationalized in terms of a strong inductive effect of the negatively-charged $B_{10}H_{10}^{-2}$ polyhedron.

Another series of ligands which are commonly attached to the $B_{12}H_{12}^{-2}$ and $B_{10}H_{10}^{-2}$ systems are electrically neutral and form co-ordinate covalent bonds with a polyhedral boron atom from which an H^- ion has been removed. The formal positive charge associated with the co-ordinated ligand serves to reduce the total negative charge of the substituted ion by one unit. The following series of novel reactions of the $B_{10}H_{10}^{-2}$ ion [16] illustrates this. (Diazotization does not occur with the $B_{12}H_{12}^{-2}$ ion, but the carbonyls $B_{12}H_{11}CO^-$ and $B_{12}H_{10}(CO)_2$ can be prepared by other routes.)



In these substitutions it is not always possible to predict whether the substitution will be apical or equatorial. Highly energetic electrophiles tend to give equatorial substitution with $B_{10}H_{10}^{-2}$ and to react readily with $B_{12}H_{12}^{-2}$ as well. Less reactive electrophiles, such as φN_2^+, give apical substitution of $B_{10}H_{10}^{-2}$ and do not react with $B_{12}H_{12}^{-2}$.

Both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have been completely halogenated [17] and the perhalogenated ions exhibit extremely high thermal stabilities. Derivatives of $B_{10}H_{10}^{-2}$ have also been halogenated, with removal of all the remaining hydrogen atoms.

$$8Cl_2 + B_{10}H_8(CO)_2 \rightarrow B_{10}Cl_8(CO)_2 + 8HCl$$

The $B_{10}Cl_{10}^{-2}$ ion is inert to strong bases, Grignard reagents, and silver ion at 100° [17]. Photochemical substitution reactions are, however, known [18].

$$B_{10}Cl_{10}^{-2} + CN^- \xrightarrow{h\nu} B_{10}Cl_9CN^{-2} + Cl^-$$

Oxidation of $B_{10}H_{10}^{-2}$ in aqueous solution [13] produces the $B_{20}H_{18}^{-2}$ ion (figure 4).

$$2B_{10}H_{10}^{-2} + 4Fe^{+3} \rightarrow 4Fe^{+2} + 2H^+ + B_{20}H_{18}^{-2}$$

Reduction of $B_{20}H_{18}^{-2}$ with sodium in liquid ammonia produces a $B_{20}H_{18}^{-4}$ ion which resembles two $B_{10}H_9\cdot^{-2}$ ions linked through a pair of equatorial boron atoms by a 2-centre electron pair bond [19]. This particular $B_{20}H_{18}^{-4}$ ion (e^2) has been converted to two other isomeric $B_{20}H_{18}^{-4}$ ions (ae and a^2) by acid-catalysed rearrangement (figure 5) which appears to proceed through isomeric $B_{20}H_{19}^{-3}$ intermediates. (e^2 represents linkage through two equatorial atoms, a^2 through two apical atoms, and ae through one of each.) The $B_{20}H_{19}^{-3}$ ions probably contain a B—H—B$^+$ bridge bond which connects the two $B_{10}H_9\cdot^{-2}$ components [19]. The most stable $B_{20}H_{18}^{-4}$ isomer appears to contain an a^2 bond

$$B_{20}H_{18}^{-2} \underset{Fe^{+3}}{\overset{2e^-}{\rightleftharpoons}} \left[B_{20}H_{18}^{-4} \underset{\text{Three isomers}}{\overset{H^+}{\rightleftharpoons}} B_{20}H_{19}^{-3} \right]$$

The reaction of $B_{20}H_{18}^{-2}$ with strong bases such as hydroxide or alkoxide ions forms substituted $B_{20}H_{18}^{-4}$ ions [20] that exhibit the reactions of the unsubstituted ion.

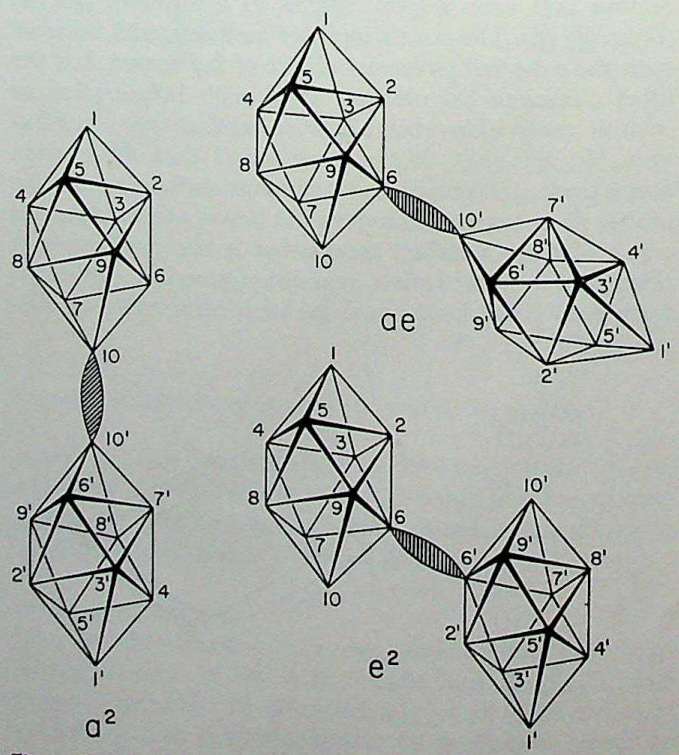


Figure 5 Structures of the three isomeric $B_{20}H_{18}^{-4}$ ions with hydrogen atoms removed.

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$$B_{20}H_{18}^{-2} + 2OH^- \rightarrow H_2O + B_{20}H_{17}OH^{-4}$$

The derivative chemistry of the B_{20} ions has not been extensively explored, nor has the chemistry of $B_6H_6^{-2}$, $B_9H_9^{-2}$, or $B_{11}H_{11}^{-2}$.

W. N. Lipscomb and his co-workers pointed out [3] that polyhedral species such as $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$, and the carboranes might rearrange by thermal distortion and interconversion of labelled vertices. Such rearrangements would interconvert isomeric derivatives and carboranes. Many of these intramolecular rearrangements have been observed in the carborane series and are described later. Little information is available concerning the rearrangement of B_{10} and B_{12} polyhedra, although $B_{10}H_8[N(CH_3)_3]_2$, $(CH_3)_2SB_{10}H_8N(CH_3)_3$, and $B_{10}H_8(CN)_2^{-2}$ have been converted to isomers by heating strongly [21]. Activation energies higher than 37 kcal/mole have been observed [21], which explains why rearrangements do not occur during substitution reactions.

Carboranes

Preparation

There is need for further research into carborane preparation. The isomers of the icosahedral $B_{10}C_2H_{12}$ are relatively easily prepared, but the starting material is $B_{10}H_{14}$, which is expensive to make on a small scale. Although at least one isomer of each of the lower carboranes has been prepared, the yields are often poor.

The 1,2-$B_{10}C_2H_{12}$ carborane and many of its carbon-substituted derivatives are readily obtained from $B_{10}H_{14}$ and an acetylene in the presence of a ligand such as diethyl sulphide [22, 23]. As in the case of $B_{10}H_{10}^{-2}$ formation from $B_{10}H_{14}$, a $B_{10}H_{12}(\text{ligand})_2$ compound appears as an intermediate. Diacetylene gives the carbon-carbon linked *bis*-1,2-carborane [24].

$$B_{10}H_{14} + 2R_2S \rightarrow H_2 + B_{10}H_{12}(R_2S)_2$$
$$B_{10}H_{12}(R_2S)_2 + HC{\equiv}CH \rightarrow H_2 + 1,2\text{-}B_{10}C_2H_{12} + 2R_2S$$

The 1,2-dicarbaclovododecaborane (12) system easily rearranges to the 1,7-isomer at 450° [25]. At temperatures near 700°, the 1,12-isomer is obtained in low yield [26]. These rearrangements are further examples of polyhedral isomerization reactions and a cubo-octahedron has been suggested [3] as an intermediate or transition state in the 1,2- to 1,7-isomer rearrangement. The 1,12-isomer cannot be formed by such a pathway and a less obvious mechanism must be involved.

Degradation of 1,2- and 1,7-dicarbaclovododecaborane (12) and their derivatives with a base produces, respectively, a quantitative yield of the 1,2- and 1,7-$B_9C_2H_{12}^-$ ions, [27].

$$B_{10}C_2H_{12} + C_2H_5O^- + 2C_2H_5OH \rightarrow B_9C_2H_{12}^- + B(OC_2H_5)_3 + H_2$$

The boron atoms that are closest to both carbon atoms in 1,2- and 1,7-$B_{10}C_2H_{12}$ are removed to generate icosahedral fragments with an open pentagonal face. The twelfth hydrogen atom has not been located. The $B_9C_2H_{12}^-$ ion derived from 1,2-$B_{10}C_2H_{12}$ contains the two carbon atoms as nearest neighbours in the open face, and the corresponding ion from the 1,7-$B_{10}C_2H_{12}$ is identical, except that the two carbon atoms in the pentagonal face are separated by a single boron atom. Both isomeric $B_9C_2H_{12}^-$ ions are converted in high yield to the same $B_9C_2H_{11}$ carborane [28] when treated with anhydrous acids and heated to 150°.

$$B_9C_2H_{12}^- \xrightarrow{H^+} B_9C_2H_{13} \xrightarrow[150°]{-H_2} B_9C_2H_{11}$$

Chromic acid oxidation of the $B_9C_2H_{11}$ carborane yields a $B_7C_2H_{13}$ species [29] which is an intermediate in the formation of 1,6-$B_8C_2H_{10}$, $B_7C_2H_9$, and 1,7-$B_6C_2H_8$ [30]. The pyrolysis of $B_7C_2H_{13}$ provides high yields of 1,7-$B_6C_2H_8$ and 1,6-$B_8C_2H_{10}$. The yield of $B_7C_2H_9$ is substantially lower.

$$B_9C_2H_{11} \xrightarrow{H_2CrO_4} B_7C_2H_{13} \xrightarrow{200°} 1,7\text{-}B_6C_2H_8 + B_7C_2H_9 + 1,6\text{-}B_8C_2H_{10}$$

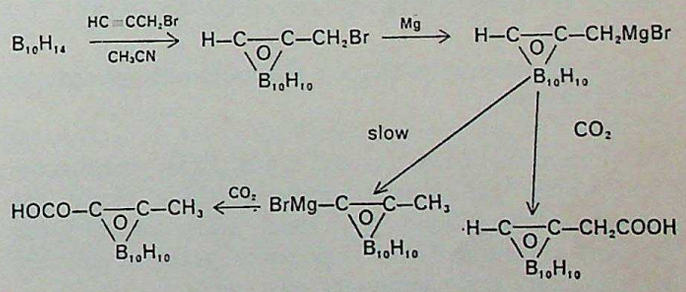
Near 350°, the 1,6-$B_8C_2H_{10}$ carborane quantitatively rearranges to the 1,10-isomer [30].

The reaction of B_5H_9 and acetylene in a silent electrical discharge [31] produces two isomers of octahedral $B_4C_2H_6$, and also a $B_5C_2H_7$ and a $B_3C_2H_5$ that probably contains carbon atoms at positions 1 and 5. Improved methods, using $B_4C_2H_8$ intermediates, are now available [32] for the preparation of the lower carboranes.

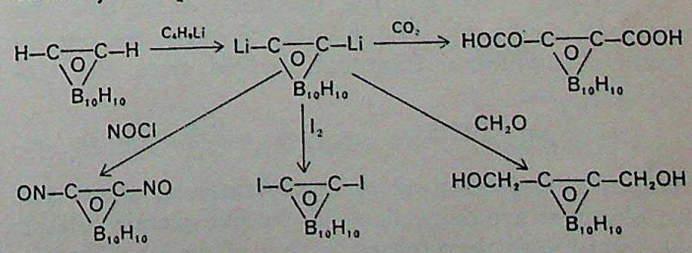
Reactions

As it is difficult to prepare the lower carboranes, very little is known about their chemistry. However, the 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes and their derivatives have been examined in some detail. Both carboranes share many of the same reactions and they function as strong electron-withdrawing substituents when attached through their carbon atoms to organic functional groups [33].

Carbon-substituted $B_{10}C_2H_{12}$ carboranes have been prepared in two ways—by including functional groups in the acetylenic starting material, and by organometallic reactions at the carborane carbon atoms. The former method is convenient for the preparation of the bromomethyl, aryl, alkenyl, and alkynyl derivatives, and certain esters which are useful synthetic intermediates.



The hydrogen atoms attached to the carbon atoms of the 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes are easily replaced with lithium by alkyl lithium reagents and the resulting dilithio derivatives serve as valuable intermediates in subsequent reactions with electrophilic reagents and carbonyl compounds.



Reactions of this type have led to a vast number of organo-functional derivatives as well as several thermally stable polymer systems with siloxane linkages [34].

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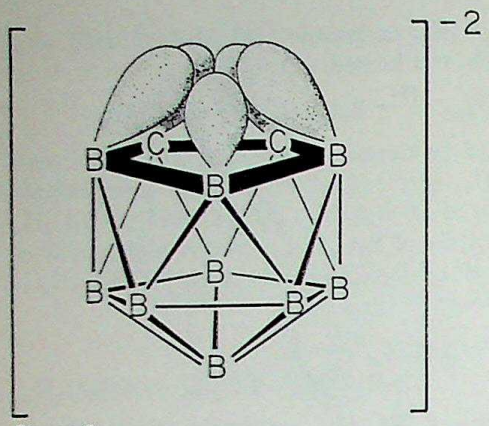

Figure 6

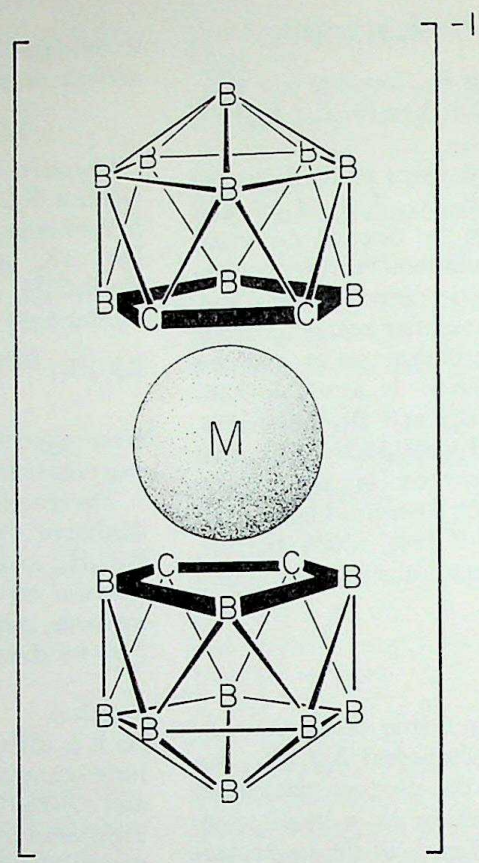

Figure 7

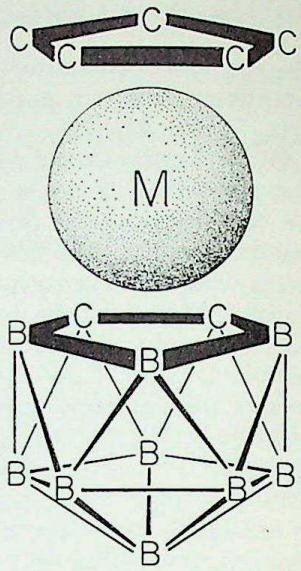

Figure 8

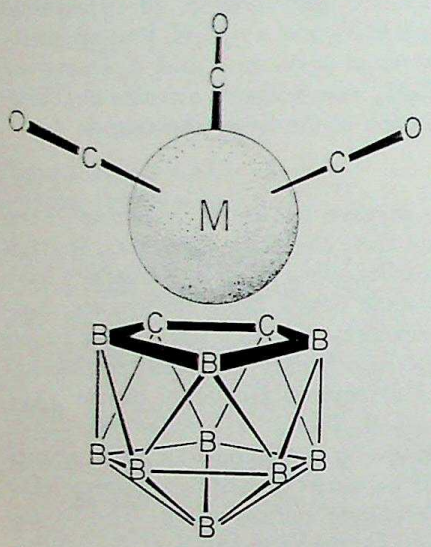

Figure 9

Figure 6 Structure of $B_9C_2H_{11}^{-2}$ ion with hydrogen atoms removed and showing sp^3 atomic orbitals directed toward vacant vertex.

Figure 7 Structure of $(\pi\text{-}B_9C_2H_{11})_2\,\overline{M}$ species with hydrogen atoms removed.

Figure 8 Structure of $(\pi\text{-}B_9C_2H_{11})Fe(\pi\text{-}C_5H_5)$ with hydrogen atoms removed.

Figure 9 Structure of $(\pi\text{-}B_9C_2H_{11})Re(CO)^-_3$ with hydrogen atoms removed.

Chlorination of the 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes yield highly chlorinated products which retain the carbon-hydrogen bonds [35]. Such materials are being explored as intermediates for polymer synthesis, and they are thermally and chemically very stable.

Carbametallic boron hydride derivatives

The challenge of combining the transition metals with the boron hydrides to produce new hybrid species has been partially fulfilled [6] by the recent discovery and structural confirmation of 'sandwich' bonding between the $B_9C_2H_{11}^{-2}$ ion [6] and transition metal ions (for example, figure 7). The $B_9C_2H_{11}^{-2}$ ion is an eleven-particle icosahedral fragment derived from the 1,2-$B_9C_2H_{12}^-$ ion.

$$1,2\text{-}B_{10}C_2H_{12} \xrightarrow{\text{degrade}} 1,2\text{-}B_9C_2H_{12}^- \xrightarrow[-H_2]{NaH} B_9C_2H_{11}^{-2}$$

Simplified molecular orbital considerations indicate that six electrons are delocalized in the five atomic orbitals associated with the pentagonal face of the ion. The disposition of these delocalized electrons (figure 6) is responsible for the observed 'sandwich' bonding, since a very similar situation arises in the metallocene precursor, $C_5H_5^-$. Thus two $B_9C_2H_{11}^{-2}$ ions readily combine with transition metal ions such as Fe^{+2} and Co^{+3} which contain six *d*-electrons. They produce filled orbital sandwich species (figure 7).

$$2B_9C_2H_{11}^{-2} + FeCl_2 \rightarrow (\pi\text{-}B_9C_2H_{11})_2Fe^{-2} + 2Cl^-$$

The iron complex is analogous to ferrocene and may be reversibly oxidized to the Fe^{+3} ferricenium ion analogue [6].

$$(\pi\text{-}B_9C_2H_{11})_2Fe^{-2} \leftrightharpoons (\pi\text{-}B_9C_2H_{11})_2Fe^- + e^-$$

Mixed sandwich species have also been prepared [36]. These carry the conventional $C_5H_5^-$ ion on one side of the metal ion and the $B_9C_2H_{11}^{-2}$ ion on the opposite side (figure 8). Their structure has been confirmed by X-ray diffraction studies [37].

Rhenium and manganese bromopentacarbonyls react with the $B_9C_2H_{11}^{-2}$ ion to produce carbonyl derivatives [38] that are analogous to the well known $\pi\text{-}C_5H_5Re(CO)_3^-$ and $\pi\text{-}C_5H_5Mn(CO)_3^-$ metallocenes. Again, the sandwich bonding associated with the completion of the carborane icosahedron by a metal atom has been confirmed by X-ray diffraction studies of the rhenium system (figure 9).

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The $B_9C_2H_{11}^{-2}$ complex ions appear to be more stable than the corresponding $C_5H_5^-$ analogues and it may be possible to produce a large number of derivatives. Electron-spin resonance studies [39] with (π-$B_9C_2H_{11}$) Fe(π-C_5H_5) indicate a bonding situation that agrees with W. Moffitt's treatment [40] of the ferrocene molecule.

Conclusions

The discovery of polyhedral ions and molecules derived from the boron hydrides suggests that this type of 'cluster chemistry' may be expected to arise in other parts of the Periodic Table. We may expect that, in view of the great interest that has been aroused in this new field, increasing attention will also be devoted to the simultaneous combination of boron and other elements in polyhedral structures. In addition, the demonstrated aromatic properties of the boron hydride systems suggest that important applications may in time emerge. It is still too early to predict what these will be, but fields which suggest themselves are advanced polymer technology, pharmaceuticals, energy-conversion devices, and electronics. Future application will, however, depend ultimately on the cost of the boron hydrides employed as starting materials. At present this is high and the development of new and cheaper routes for the economic conversion of borax to boranes remains a challenging and commercially important problem.

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Stabilizing mine dumps with vegetation

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A. L. James

The waste materials from the gold mines of the Witwatersrand in South Africa have accumulated over the years until they have formed large dumps, dangerously liable to erosion by air and water. It was not possible to stabilize these dumps by physical means, and this article describes experiments using vegetation for this purpose. It also describes the methods used to alter the chemical nature of the dumps so that the vegetation would form a permanent establishment.

Mining operations on the Witwatersrand goldfield during the past seventy years have resulted in an accumulation of residues that have a surface area exceeding 25 000 acres, and the golden-coloured dumps have become a characteristic feature of the area, standing out in a striking manner against the flat terrain in which they are situated. The gold deposits in this area are contained in a narrow band of conglomerate embedded in quartzite, and the dumps consist almost entirely of finely ground rock from which gold and sometimes uranium has been removed. It has been realized for some time that they would have to be stabilized against erosion by wind and water, and attempts to do this have been made ever since they attained appreciable size, more than fifty years ago.

The idea of growing trees and grass on the dumps has always appealed to men living and working on the mines and in the towns that have grown up along the reef, but early plantings met with no appreciable or widespread success. All available information concerning these attempts to use vegetation was collected and studied by John Phillips in 1932, and he then directed further experiments with various plant species. The results were disappointing and discouraged any idea of rapidly establishing such a cover [1]. For the next twenty years, attempts to stop dust from blowing off the dumps were confined to physical methods, none of which was entirely satisfactory.

By 1953, the problems posed by the erosion of the dumps had become much more serious, and all known methods of stabilization were reviewed. Three years later it was finally decided that a cover of vegetation would be the most satisfactory means of permanently stabilizing the dump surfaces, if this could be established.

Preliminary investigations

Different methods of disposing of the tailings—the residues—have led to the production of two kinds of dump, each of which poses its own problems.

Sand dumps are heaps of the ground rock from which the gold has been recovered. They may cover areas up to 100 acres, and reach heights of about 200 feet. 'Slimes dams' are built up of more finely ground material which is suspended in water to form slimes, and then pumped through pipes to the area where it is to be stored. A low wall of dried slimes is constructed round the storage area, which is then filled with slimes. Water is drained off, and the solid material settles out. As the dam fills the wall is raised, and eventually the dump may reach a height of about 100 feet with sides forming an angle between 30° and 50° with the ground and a flat top with an area of up to about 400 acres. Both kinds of dump can be seen in figure 1.

The establishment of a permanent cover of vegetation involves not merely growing plants. It necessitates bringing into being a plant community that will maintain itself indefinitely without further attention or artificial aid, such as irrigation. Such permanence could be achieved most advantageously by selecting species adapted to growth, spread, and reproduction under the severe conditions provided both by the nature of the dump material and by the exposed situation on the dump surfaces above the level of the surrounding terrain. This possibility was investigated, in spite of both the failure of the local flora to invade the dumps in the course of fifty years and the discouraging results obtained in earlier attempts. Conditions, particularly on the sand dumps, were considered similar in many ways to those in semi-desert areas, and an expedition was made to the Kalahari desert to examine the vegetation and bring back material for test. The vegetation in such areas persists under adverse conditions, but it generally grows and spreads only slowly; the most interesting species encountered was *Imperata cylindrica*, which was growing freely in dry sand and spreading over a considerable area by means of tough rhizomes. However, when tested on a mine dump, it made little growth for two years, although it spread quite extensively afterwards.

Seeds of plants used for desert reclamation, for stabilizing sand dunes, or for covering the sides of deep cuttings in arid areas, were obtained from various parts of the world; but only Pyp grass (*Erharta gigantea*) and Marram (*Ammophila arenaria*) were at all successful on the dumps. Pyp grass grows well in very exposed situations where it is continually being covered by fresh drift sand but, at any rate on the dumps, it dies out when the surface has been stabilized. It thus has only limited application in the establishment of a permanent cover. None of the leguminous plants tested were successful. However, the seed of varieties of clover (*Trifolium* spp.) and Vetch (*Vicia*) was irradiated to induce mutation, and then sown on a slimes dam: several interesting plants from this seed grew well.

After some hundreds of species had been tested, it became clear that the exotic or uncommon plants best adapted for growth on the dumps would not provide a satisfactory solution to the problem. They grew and spread slowly, so that there would always be difficulties in raising sufficient seed for the plants to be used on a large scale. It was decided therefore to concentrate on the possibility of producing conditions in the surface layers which would enable the more tolerant species in commercial use in South Africa to be grown, and to use

A. L. James, *M.A., D.Phil.*

Was born in 1904 and educated at Oriel College, Oxford. His first research was in plant pathology at Exeter University and in the Division of Botany in Pretoria. After the war he became Director of the biological and chemical research laboratory of the South African Chamber of Mines, a post he held until 1964. He is now a research consultant to the Transvaal and Orange Free State Chamber of Mines.

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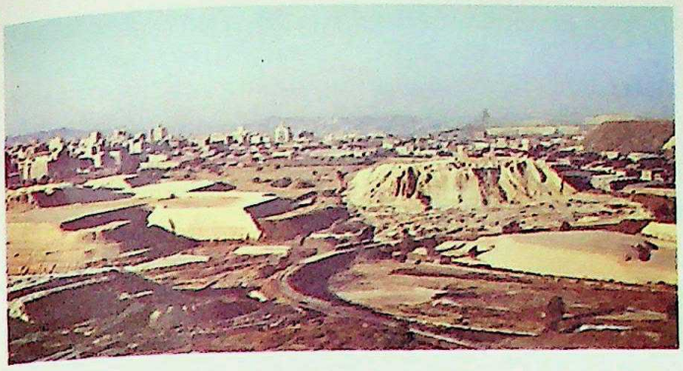

Figure 1

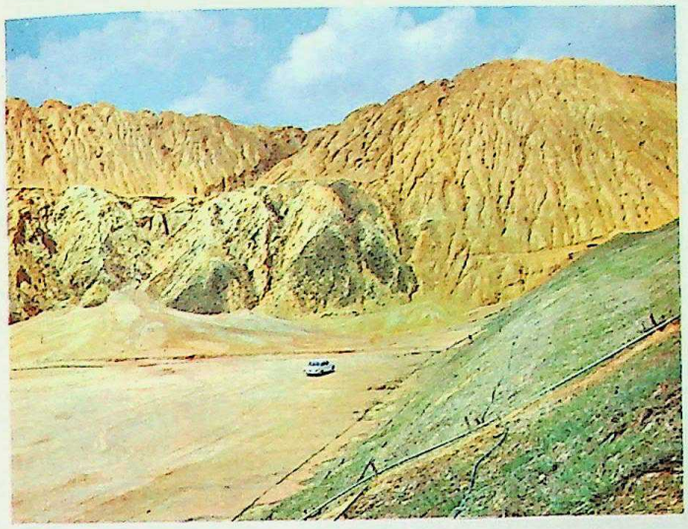

Figure 2

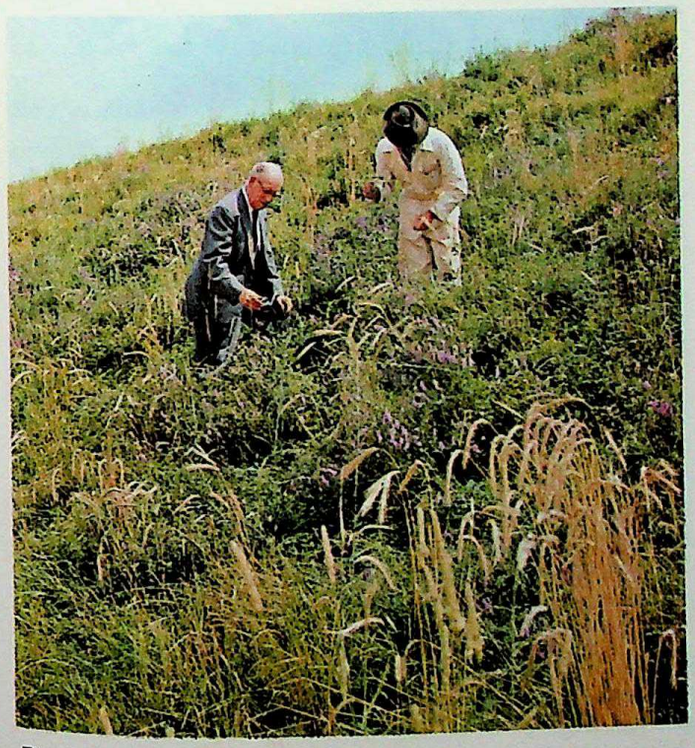

Figure 3

Figure 4

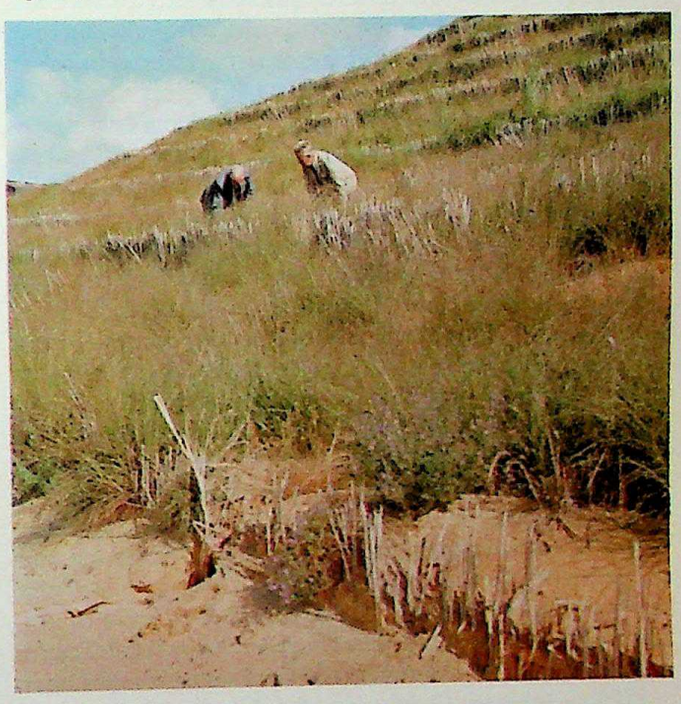

Figure 5

Figure 6

Figure 1 Mine dumps south of Johannesburg.

Figure 2 Mist spray in action on a slimes dry wall.

Figure 3 Part of the slimes dam wall shown in figure 2 after completion of the operation.

Figure 4 Liming and seeding the paddocks.

Figure 5 Grass cover emerging on the side of a sand dump. The grass is mainly *Eragrostis curvula*.

Figure 6 The top of a slimes dam four years after seeding.

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the most suitable of these plants. The danger inherent in such a system on a large dump is that conditions in the surface skin may, in the course of years, revert gradually to the original unfavourable state, when the vegetation would die off. The method finally adopted reduces this possibility to a minimum.

Growth in altered conditions

A wide range of species can be grown, although not all of them persist, if the pH value of the dump material is raised to 5·0 or slightly higher and nutrients are supplied. For instance, Kikuyu grass (*Pennisetum clandestinum*) appears ideal for the purpose, as it grows and spreads rapidly at first, and makes a thick tough cover. However, it dies off unless supplied periodically with additional water and nutrients.

Seed of most of the species finally selected was commercially obtainable, but a few species not in commercial use proved so effective that a nursery was established to provide supplies. *Cynodon plectostachyus* covers an area by vegetative reproduction better than does any other grass tested, rapidly producing a dense network of stolons from which individual plants subsequently arise. *Pennisetum macrourum* and pampas grass (*Cortaderia selloana*) were also so useful that they were grown in the nursery.

A small number of species was selected for field trials and sown as a mixture. They included plants having the desired habits of growth, modes of reproduction, and other characteristics to produce a cover that would give adequate protection against erosion by both wind and water. A mixture of grasses was used because a pure stand of a species does not persist on mine dumps as well as a mixed stand. The material and situation varied, so that different grasses were successful on different dumps, and as the individual factors involved in each case are not known, a mixture of seed is sown.

The following species were used:

Cover grasses: *Bromus catharticus, Agrostis tenuis, Dactylus glomerata, Eragrostis curvula, Holcus lanatus, Poa pratensis, Phalaris tuberosa, Cynodon dactylon, Cynodon plectastachyus, Chloris gayana, Ehrharta calycina, Pennisetum macrourum, Cortaderia selloana.*

'Nurse' plants: Oats (*Avena sativa*), Barley (*Hordeum sativum*), Rye (*Secale cereale*).

Legumes: Clover (*Trifolium* spp.), Hairy Vetch (*Vicia villosa*), Lucerne (*Medicago sativa*).

Trees: *Acacia baileyana, Acacia melanoxylon.*

A final trial with the selected species on a dump on which the acidity had been corrected with lime and the necessary nutrients had been added, resulted in the production of a satisfactory cover. A mechanized unit was therefore assembled to carry out the same process on several more dams. It was possible to work at a rate of about 15 acres a day, after which the area received no further attention. The results were so encouraging that the problem appeared to be solved. Individual mining companies also carried out experiments on the same lines, in some cases with considerable success [2].

Large-scale tests

The mechanized unit then moved to the East Rand, and the same methods were used at two mines. The great variation between dams and different parts of a single dam, so far as establishing vegetation is concerned, here became fully apparent for the first time. On one dam the procedure was fairly successful; on another, about 400 acres in extent, it was partially successful in a few places but failed completely over most of the area; on others, it was completely unsuccessful.

The unexpected failures occurred because the pH value of the slimes remained low even after the addition of lime in quantities that had been considered sufficient to neutralize the acidity present. Further addition of lime to test areas failed to provide a suitable pH for plant growth, and it became clear that this method of raising the pH value was satisfactory only on dumps of low or moderate acidity.

The slimes as deposited are alkaline in reaction, but the Witwatersrand ores contain iron pyrites in varying amount, and oxidation of the pyrite, often accelerated by bacteria, causes a gradual accumulation of acidity in the surface layers of the dump. Acidification occurs to depths of about 6 feet, with a zone of maximum acidity about 12 inches below the surface. The pH value of the material near the surface varies from dump to dump and place to place, depending on how much pyrite is present and the extent to which oxidation has occurred. Acidities up to 2 per cent and pH values as low as 1·5 are encountered, sometimes over areas many acres in extent.

There is some evidence that the acidity moves downwards, particularly during rain, but this movement is halted or reversed by evaporation from the surface. It was decided to try to maintain the downward movement until the acidity reached a depth at which it would enter the alkaline body of the dam, or at any rate not return to the surface during any combination of weather conditions that could be anticipated.

It is neither practicable nor desirable to flood the top of a slimes dam with water, since prolonged flooding compacts the material and produces conditions that are very unfavourable for plant growth. However, the downward movement of the acidity can be encouraged by an extremely fine spray of water, which forms a mist over the surface and retards evaporation. The rate of deposition of water must not exceed the rate at which it can infiltrate into the slimes. The permeability of these is very low, and in practice no system could be devised which deposited water evenly over a large area at a sufficiently low rate. The nearest approach to the ideal was obtained by using fine jets surmounted by striker plates inserted at intervals along piping laid in parallel rows. Observations of the movement of acidity under these conditions confirmed the conclusions based on laboratory studies [3], and showed that the zone of high acidity could be moved to a sufficient depth, usually within a period of three to four weeks.

As high acidity could now be dealt with, it was possible to establish growth on the sloping sides of the slimes dams: these are more acid than the tops and had hitherto proved impossible to vegetate. Figure 2 shows a mixed dump. The flat area is the top of a slimes dam, the slope on the right an internal wall to a higher level, and in the background is a sand dump. Work is in progress on the internal wall, and the mist spray can be seen as a faint haze above the surface. Since the acid moves down faster than the roots of the seedlings, the area can be sown before the spray is started, and the green colour of the emerging vegetation can be seen. The area shown in figure 3 is part of the same wall where the operation has been completed.

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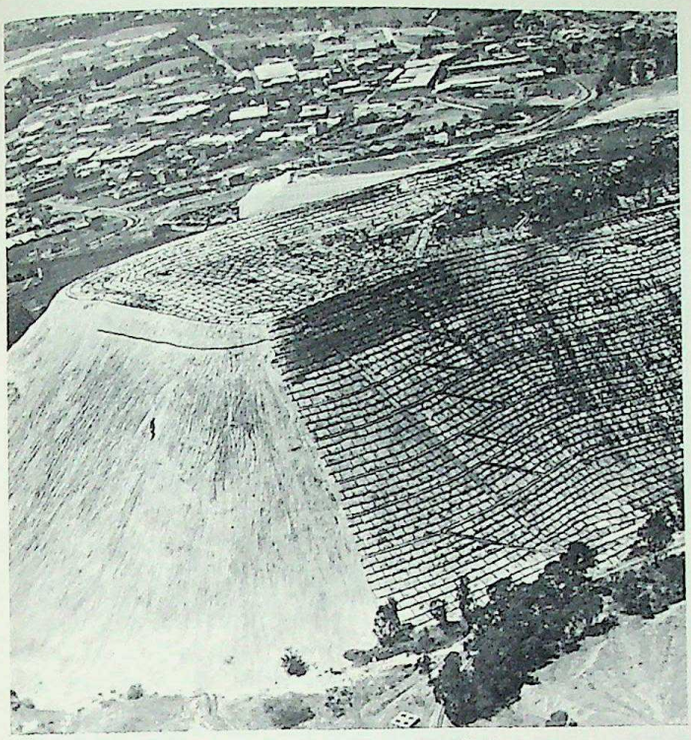

Figure 7 Establishing vegetation on a sand dump.

Figure 8 Mine dump showing various stages of establishment of vegetation.

Even when suitable plant species have been selected and techniques have been developed for preparing the material for their growth, sand dumps still pose problems. This is because the surface moves in wind, and because it is difficult to work on the steep slopes of loose sand. Unless the surface is stabilized temporarily, work on the establishment of vegetation can be lost in a few hours by being buried under several feet of sand or by the surface being blown away. In addition, the abrasive action of ground rock blown across the surface will strip plants to a bare stem.

There are several ways of achieving temporary stabilization, but the most effective and economic method is provided by a system of low windbreaks made with cut stems of reeds (*Phragmites communis*). The area is divided into small paddocks whose size is determined by the slope of the ground, the windbreaks are erected, and the various procedures leading to seeding and mulching can then be carried out. The windbreaks afford excellent protection for the seedlings until they have grown sufficiently to become stable. Figures 4 and 5 show steps in this procedure. Figure 7 is a general view of a sand dump on which vegetation is being established.

The ultimate objective is to bring into being a self-supporting plant community. What has been achieved so far is the establishment of an initial cover of vegetation composed of species able to grow and persist, at any rate for a time, on the dumps after the pH value has been raised and nutrients supplied which are not normally present. Few, if any, of the plants would survive if conditions reverted to normal in what is only a thin skin on the surface.

From this point of view, moving acidity from the surface layers down to a depth from which it will not return is sound, provided the technique is not applied until most of the iron pyrites in the surface layers has been oxidized. There is so far no sign of the acidity reappearing after vegetation has been established.

Figure 8 illustrates the success that has been achieved. In the foreground is a sand dump on which an initial cover of vegetation was established while the methods were being developed about three years ago. The outline of experimental plots is clearly visible from the air, although no longer easy to find in the tall grass. The tops of the two slimes dams beyond were used for experiments, and in the background there is a slimes dam the top of which has a complete cover, while work has begun on vegetating the sides.

The initial vegetation has a beneficial effect on the environment. The dump material initially contains no organic matter; there is no microflora other than bacteria that oxidize iron and sulphur, and no nitrogen is detectable by chemical analysis. The fast-growing annuals and the legumes included in the seed mixture produce plant debris after a short time, and this is continually added to. After a year or two, there is a perceptible improvement in the surface layers of material. As a result of the improved conditions and the shelter provided by the vegetation, species from the flora of the surrounding countryside begin to appear on the dumps—the first to do so usually being members of the Compositae.

Some of the grasses introduced die out and the vegetation after three or four years may consist mainly of a few species which have flourished and spread, but there is so far no indication that a cover of vegetation will not be maintained. Figure 6 shows the top of one of the first slimes dams dealt with which has received no attention since being seeded four years ago. It seems likely that in the course of years the composition of the cover may change until a flora in equilibrium with the environment emerges.

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Chemical problems in semiconductor research

Albrecht Rabenau

Elements, germanium and silicon in particular, have been used as semiconductors for some time, and their behaviour is well understood in terms of the 'band theory'. The demands of technology have now led to attempts to find semi-conductors among compounds. For these purposes it is essential to be able to predict, on chemical grounds, the compounds likely to be of value, and this has proved theoretically intractable. However, it as been possible to establish empirical rules, and this article describes these and suggests the principles underlying them.

Semiconductors—a group of substances whose electrical conductivity falls between that of the true metals and that of the insulators—have become important in technology only in the last twenty-five years. Before that, the only ones of any consequence were copper oxide and selenium, in rectifiers; and lead sulphide, whose potentialities as an infra-red detector had just been appreciated. The theoretical basis for an understanding of semiconductors is the 'energy-band' model, referred to later in this article, which had been established by A. H. Wilson in 1931. However, the modern development of semiconductors did not start until the invention in 1948 of the transistor by W. H. Brattain and J. Bardeen, in the Bell Laboratories. This was possible only because of the successful production, during the war, of extremely pure germanium, which could be used to test Wilson's model. Since then, development has been rapid, and semiconductors play a very important part in modern solid-state physics. This article will deal with the interrelations between semiconductor research and solid-state chemistry.

Fundamentals

Germanium is a suitable model for describing the mechanism of conduction in semiconductors [1]. In this case, where the element crystallizes in the diamond structure, the relationships are simple—each atom is located at the centre of a tetrahedron formed by four other atoms. Two electrons, one of which is from the central atom, participate in each of the four covalent bonds. These four equivalent tetrahedral bonds are not based on the s^2p^2 ground state of the valence electrons of the group IV elements, but on an 'excited state'. This involves the hybridization of the s and p eigenfunctions to give the sp^3 hybrid.

When atoms are brought together so as to form a crystal, the discrete energy-levels of the atoms interact to form bands of permissible energy-levels (figure 1). With four valence electrons per atom, the states in the highest occupied band (the valence band) are already filled: conduction is possible when electrons are raised from the valence band into the conduction band (figure 5a). The electron density in the conduction band becomes greater as the energy gap between valence band and conduction band becomes smaller and as the temperature rises. Electrons are not the only source of conductivity: the holes arising in the valence band also make their contribution, behaving as positive charge carriers. The total conductivity is

$$\sigma = e(n\mu_n + p\mu_p)$$

where e is the elementary charge, n and p the concentration of negative and positive charge carriers, and μ_n and μ_p the associated mobilities. In the case of intrinsic conductivity, which is a characteristic property of the substance and dependent only upon the temperature, $n_i = p_i$. If the substance is not specially purified, the intrinsic conductivity is usually masked by the 'extrinsic' conductivity, caused by impurities. Thus, an element of group V, occupying the place of a germanium atom in the lattice, can release its excess valence electron, which is

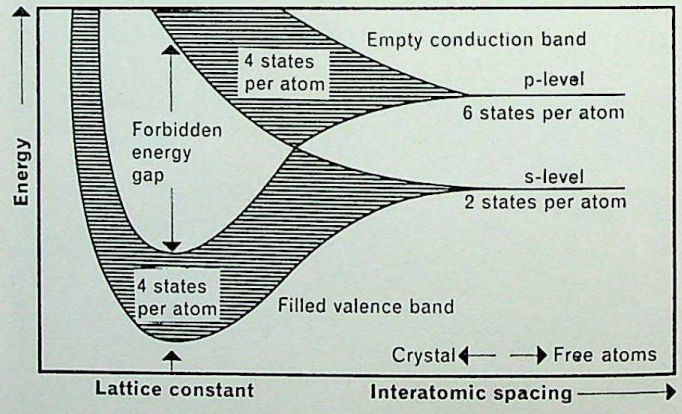

Figure 1 Schematic energy diagram for elements of the 4th group with tetrahedral structures.

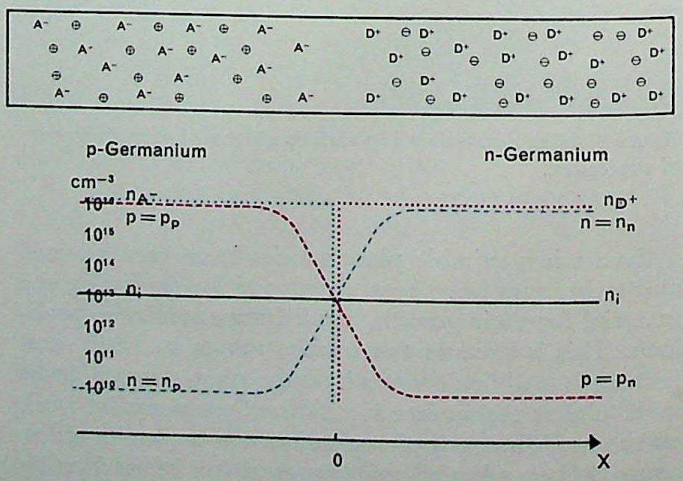

Figure 2 p-n-junction in germanium. The change of electron and hole concentration is plotted in the lower part of the figure. $np = n_i^2$ where $n_i \simeq 10^{13}$ cm^{-3} at room temperature. (A^- and D^+ are ionized acceptors and donors respectively. [1]

A. Rabenau, *Dr. rer. nat.*
Was born in Heppenheim/Bergstrasse, Germany, in 1922 and educated at the University of Heidelberg. He spent three post-doctoral years at the University of Kiel. In 1955 he joined the Philips Research Laboratories, in Aachen, where he is now Deputy Director. In 1963 he was appointed *Privatdozent* at the *Rheinisch Westfälische Technische Hochschule*, Aachen. His chief research interest is in the field of solid-state chemistry.

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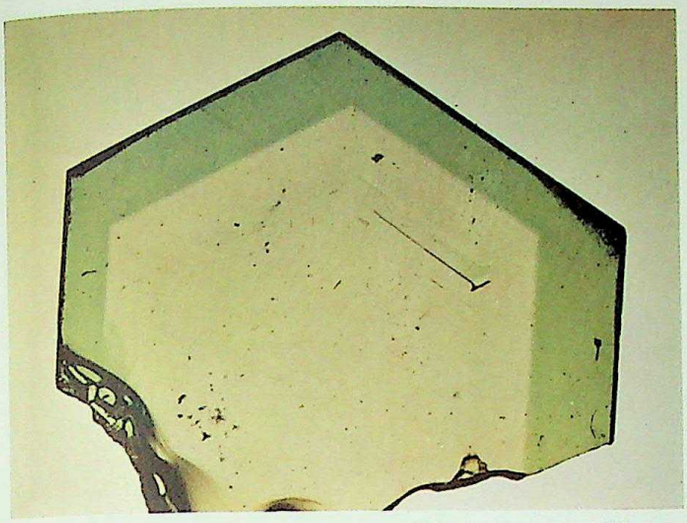


Figure 3 p-n junction in a hexagonal SiC single crystal. The conversion from p-type to n-type conductivity is induced by addition of nitrogen to the argon atmosphere during crystal growth. The n-type region is coloured green [15]. (×10)

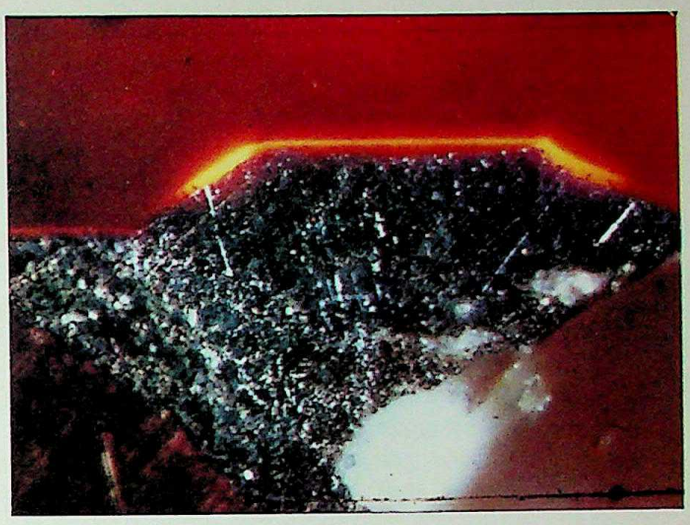
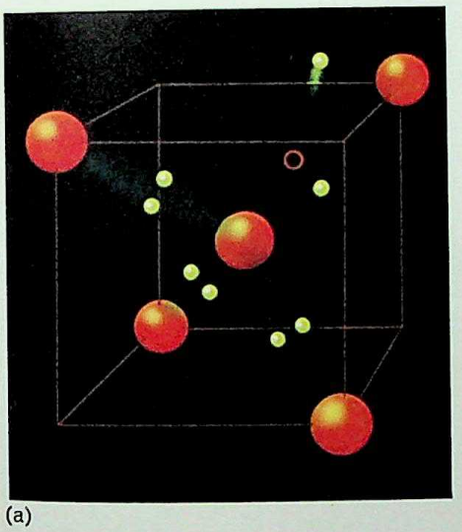


Figure 4 p-n junction in GaP exhibiting p-n luminescence when a forward current (10 mA) is flowing. The recombination of charge carriers is accompanied by the release of energy in the form of light quanta [16]. (×20)



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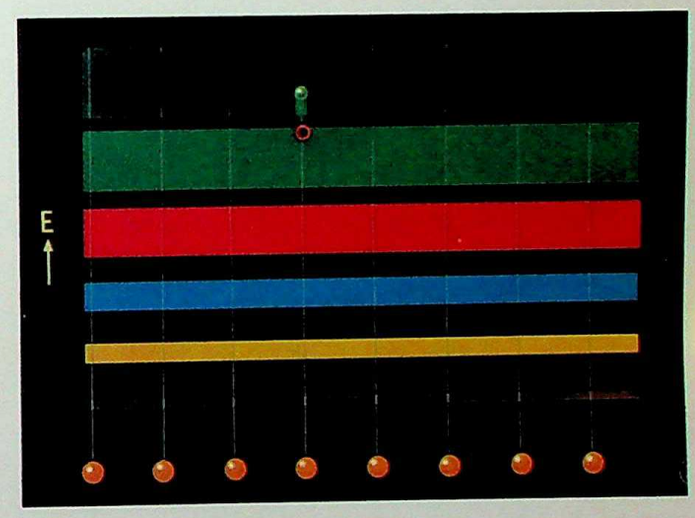

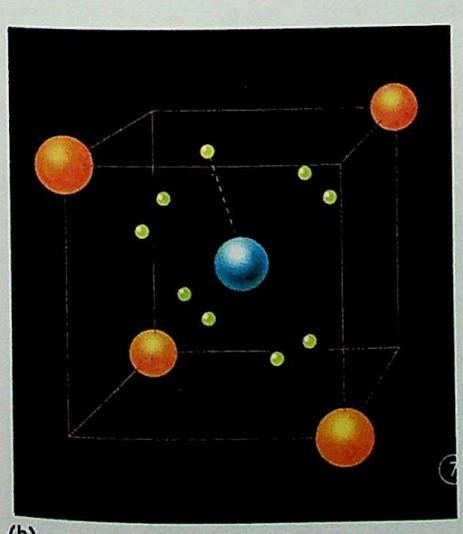

(b)

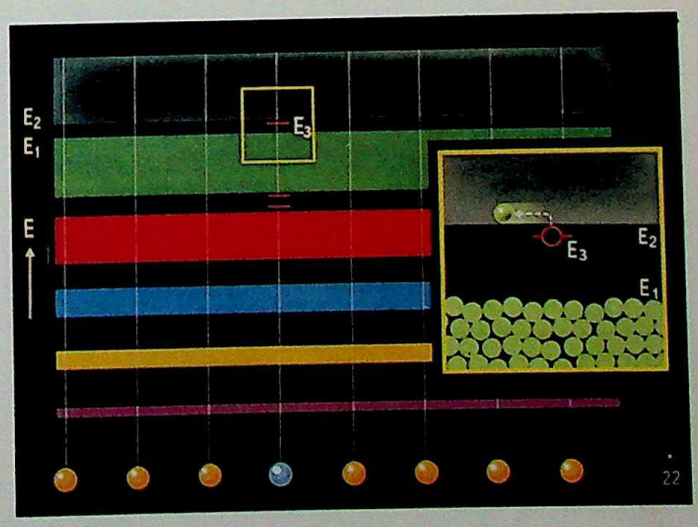

Figure 5 Types of conductivity. Chemical bond pictures (left), and energy band models (right). (a) Intrinsic conductivity. The removal of a valence electron from its electron-pair bond by thermal excitation is equivalent to the transfer of an electron from the valence band to the conduction band. (b) *n*-type conductivity. The arsenic atom with weakly bound fifth valence electron, if substituted for a germanium atom, acts as donor.

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only weakly bound, to the conduction band. Substances such as these act as electron donors and lead to electron-conduction—*n*-conduction (figure 5b). In a similar way, electron holes, which occur as a result of the introduction of group III elements, give rise to hole-conduction—*p*-conduction. Because of their tendency to trap electrons from the valence band, group III impurities are known as acceptors. Practically all semiconductor devices make use of the properties of these two types of conduction, and *p-n* junctions play a special part. A *p-n* junction is the boundary between a *p*-conducting crystal zone and an *n*-conducting one (figures 2–4).

Quantitative control of the type and concentration of charge carriers is essential throughout semiconductor technology. For this, use is made of reaction equations for charge carriers that are essentially similar to the chemical equilibrium equations for aqueous solutions [2]—ionization in solid-state semiconductors corresponds to ionization of water. The role of the hydroxyl and hydrogen ions ($H_2O \rightleftharpoons H^+ + OH^-$) is assumed by the conduction electrons and holes (lattice $\rightleftharpoons e^+ + e^-$) (table 1). Figure 6 shows one analogy between ionization and the formation of charge carriers.

The following example illustrates the exceptional demands for purity if intrinsic conduction is to be predominant at room temperature: for germanium, no more than 10^3 atoms of arsenic may be present in a crystal of 1 cm^3 that contains 10^{23} atoms. This means less than one arsenic atom to every 10^{10} germanium atoms. Such extreme purities are fortunately not always required. Nevertheless, the charge-carrier concentrations between 10^{15} and 10^{19} per cm^3 that are normally employed presuppose prior purification to give a concentration of impurity less than this. The charge-carrier concentration is controlled through 'doping' with impurities that act

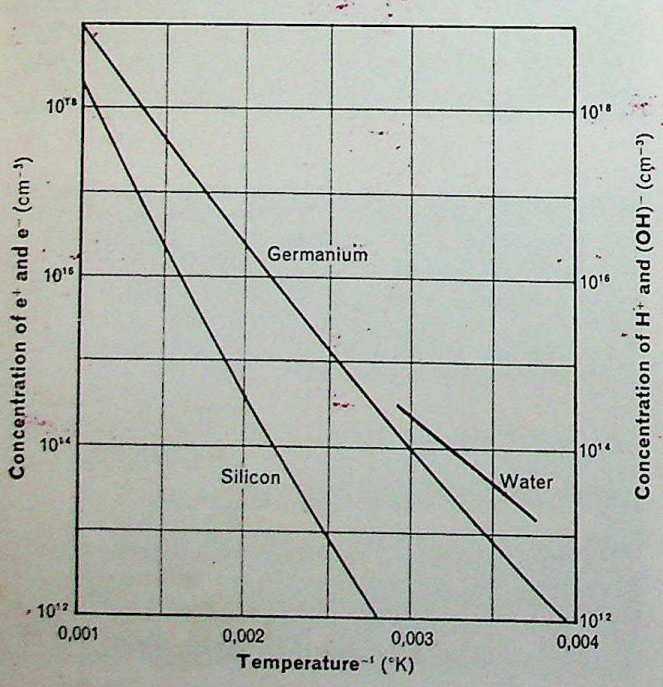
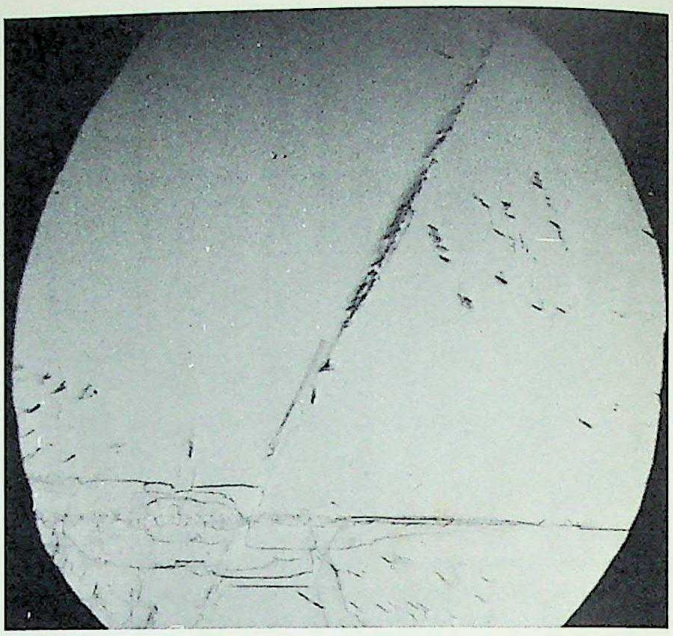
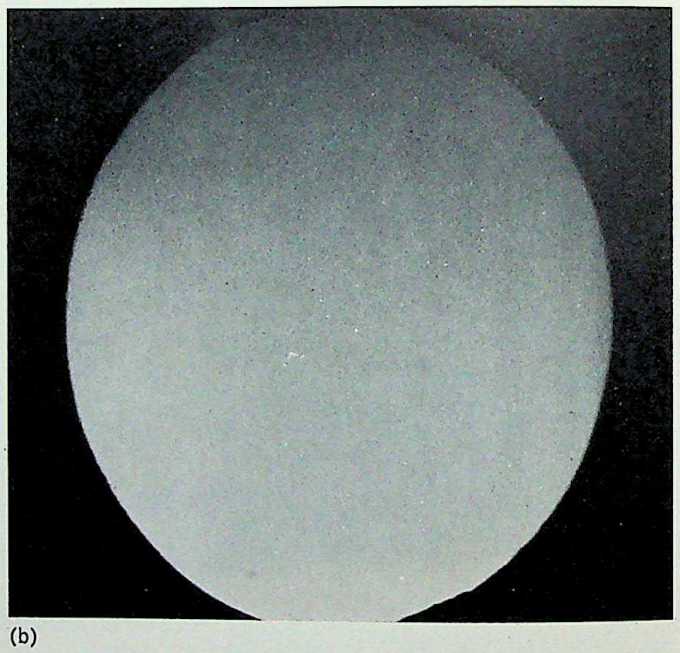


Figure 6 Temperature-dependence of the self-dissociation of water and intrinsic conductivity of silicon and germanium. The concentration of ions and charge carriers is of the same order of magnitude and varies exponentially with the temperature [2].



(a)



(b)

Figure 7 Perfect crystals show very low absorption when irradiated by X-rays under the Bragg condition. Lattice distortion in the region of a dislocation increases the absorption. The dislocations appear as shadows. (a) shows a germanium crystal containing dislocations, (b) a dislocation-free crystal. (Both × 100)

Figure 8 (right) Growth spirals in a single crystal of SiC [15]. This phenomenon is caused by screw dislocations. (× 230)

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Table I
Reactions in aqueous media and in semiconductors [2]

Aqueous solution	Semiconducting crystal
$H_2O \rightleftharpoons H^+ + (OH)^-$ $K_{H_2O} = [H^+][(OH)^-]$ $[H^+]$ and $[(OH)^-]$ $\simeq 10^{14}/cm^3$ (30°C) Self-dissociation	Ge lattice $\rightleftharpoons e^+ + e^-$ $K_{Ge} = [e^+] + [e^-]$ $[e^+]$ and $[e^-]$ $\simeq 5 \times 10^{13}/cm^3$ (30°C) Intrinsic conductivity
$NH_4OH \rightleftharpoons NH_4^+ + (OH)^-$ $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ Dissociation of acid or base	$As \rightleftharpoons As^+ + e^-$ $Ga \rightleftharpoons Ga^- + e^+$ Dissociation of donor or acceptor
Adding base or acid decreases concentration of H^+ or $(OH)^-$.	Adding donor or acceptor decreases concentration of e^+ or e^-.
$H_2 \vdots HClaq \vdots NaOHaq \vdots H_2$ $E_{volts} = \frac{RT}{F} \log \frac{[H^+]\ HClaq}{[H^+]\ NaOHaq}$ Concentration cells	$-\boxed{\text{p-type} \mid \text{n-type}}-$ $E_{volts} = \frac{RT}{F} \log \frac{[e^+]_p}{[e^+]_n}$ p-n junction

The analogies shown between reactions in aqueous solution and those in semiconductors result from the essential similarity between the hydrogen—hydroxyl equilibrium in water and the hole (e^+)—electron (e^-) equilibrium in semiconductors. Both equilibria are governed by the law of mass action.

as donors or acceptors. Provided that intrinsic conduction is not dominant, manipulation of the charge carrier concentration enables us to vary the type and magnitude of the conductivity of a semiconductor within certain limits, whereby

$$np = n_i^2$$

In addition to the height of the forbidden-energy region or band gap, the properties of a semiconductor include the mobility and lifetime of the charge carriers. Mobility and lifetime are strongly influenced not only by the purity of the substance, but by the degree of perfection of the crystal lattice—every real crystal is defective to a greater or lesser degree. The imperfections include Frenkel and Schottky defects and edge and screw dislocations (figures 7 and 8). The present state of semiconductor physics is in part a result of the great progress made in crystal growing. It is now possible to draw dislocation-free single crystals of germanium and silicon: normal crystals of these substances have dislocation densities between 10^3 and 10^5 per cm^2 of crystal cross section.

Semiconducting compounds

The use of compounds instead of elements in semiconductors leads to further difficulties. Firstly, stoichiometry must be maintained or controlled, since small deviations can lead to the development of donors and acceptors; and secondly, the number of possible atomic defects is increased. A fundamental study of semiconductor properties demands single crystals of the maximum purity and perfection, and this explains why there are no compounds, with the possible exception of indium antimonide, over which we have the same experimental and theoretical mastery as we have over the elements germanium and silicon. However, the limited number of semiconducting elements obliges us to turn to compounds, and many semiconductor devices rely upon the existence of suitable compounds with specific properties (table II).

Other applications would be practicable if semiconductors with suitable properties were available. Unfortunately, although the choice of compounds eligible as semiconductors is practically unlimited, the experimental effort required is also almost unlimited and restricts investigations to those that are the most promising. It is therefore urgently necessary to understand more about the processes that lead to a compound of definite composition and structure, and of specific properties. It is theoretically possible to solve this problem exactly with the aid of the Schrödinger equation, but even in the case of simple binary compounds, the Schrödinger equation is insoluble because of its complexity, and it appears that this state of affairs is unlikely to change in the foreseeable future. It is therefore worth while investigating the possibility of using the Periodic Table as a guide to suitable compounds, and this seems today to be the most hopeful approach. The work has produced some useful semi-empirical principles, but unfortunately the lack of adequate experimental foundations has led to a speculative treatment in the literature. It has, however, been possible to establish some working rules. From the foregoing we know that, for a compound to have the properties of a semiconductor, there must be a filled valence band separated from the next empty band by a finite forbidden-energy gap. Each rule has to consider this fact. In addition, it is important to investigate the validity of the various rules in extreme cases, for it is in fact often the exceptions that are of particular theoretical interest.

The tetrahedral structures described below are representative of those which have been most thoroughly examined and are best supported by theory.

Compounds with tetrahedral structures

Our most detailed knowledge is of the tetrahedral structures, as represented by group IV elements such as silicon and germanium. Most of the compounds listed in table II that have found application as semiconductors also have this basic structure. Cubic zinc blende and hexagonal wurtzite, both natural forms of zinc sulphide, are familiar representatives (figure 9). The structure is based, in the case of zinc blende, upon a close-packed cubic arrangement of the sulphur atoms and, in the case

Table II
Semiconductor devices. Elements or compounds with tetrahedral structures are italicized

Substance	Application
Ge, Si, Se, Cu_2O	Rectifiers, diodes
Ge, Si, Se, *CdS, CdSe*	Photocells
Ge, Si, GaAs	Tunnel diodes
GaP, GaAs	Luminescence diodes
GaAs	Varactor diodes
GaAs, GaAs-GaP solid solution	Injection lasers
Ge, Si, GaAs	Transistors
PbS, PbTe	Infra-red detectors
SiC	Varistors
InAs	Hall generators
Bi_2Te_3-, Bi_2Se_3-, Sb_2Te_3-solid solutions, *Si-Ge solid solutions*, PbTe	Thermoelectric materials (including Peltier elements)

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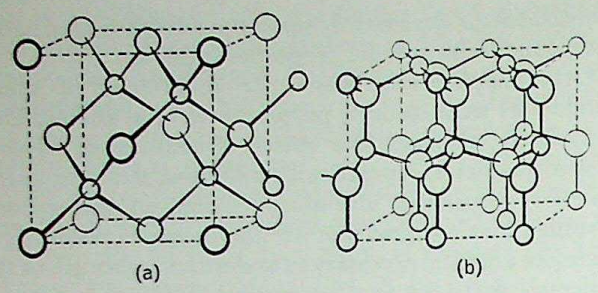

Figure 9 Crystal structures of zincblende (a) and wurtzite (b). The most important representatives of tetrahedral structures belong to these or related structures. (See also figure 14.) ○ *S* ○ *Zn*. [18]

of wurtzite, upon a corresponding close-packed hexagonal arrangement. The diamond lattice is derived from that of the zinc blende by filling all atom sites with the same element. No elemental structure is analogous to wurtzite.

V. M. Goldschmidt established in the early 1920s that a wide range of binary compounds of composition AX, whose elements are symmetrically disposed about group IV, can form tetrahedral structures. The lattice spacing is virtually the same throughout the range, which indicates that there is a special state of bonding in these compounds. They are formed between elements of groups III and V, groups II and VI, and groups I and VII. Typically, the atomic separation in the germanium (44) lattice is 2·44 Å, and in GaAs(35), ZnSe(26), and CuBr(17) it is 2·44 Å, 2·45 Å, and 2·46 Å respectively. (In this article, 44 represents both a binary compound of elements from group IV and a single element of group IV; 3_26 represents a binary compound of two atoms of an element from group III and one from group VI; and so on.) We should have expected, for purely ionic bonding, that the spacings would decrease with increasing charge of the elements. H. G. Grimm and A. Sommerfeld pointed out that the occurrence of the tetrahedral structure is connected with the concentration of valence electrons, defined as the ratio of the number of valance electrons to the number of atoms per formula unit. The Grimm-Sommerfeld rule states that a tetrahedral structure can be expected when there are four valence electrons per atom. This appears to be a necessary stipulation, but table III shows that it is not the only one, since with increasing separation in the Periodic Table of the elements of the compound, there is an increasing tendency to form the sodium chloride lattice with a co-ordination number of 6.

Table III
List of Grimm-Sommerfeld compounds [3]

1–7		2–6					
CuF ?	•	BeO	•	ZnO	•	○	•
CuCl	•	BeS	•	ZnS	CdS	HgS	MnS
CuBr	•	BeSe	•	ZnSe	CdSe	HgSe	MnSe
CuJ	AgJ	BeTe	MgTe	ZnTe	CdTe	HgTe	○
		BePo	○	ZnPo	CdPo	•	

3–5				4–4			
(BN)	AlN	GaN	InN	(CC)	SiC	—	—
BP	AlP	GaP	InP		SiSi	Si-Ge	—
BAs	AlAs	GaAs	InAs			GeGe	—
BSb ?	AlSb	GaSb	InSb				SnSn

(BN) and (CC) with tetrahedral structure are thermodynamically stable only under pressure.
Complete solid solution between Si and Ge.
▭ Tetrahedral structures.
• NaCl structure.
○ Other structure type.
— No compound

These relationships have long been known to chemists, but became of practical importance only when the semiconducting properties of the Grimm-Sommerfeld compounds became known and found practical applications. H. Welker pointed out in 1952 that the fact that the '35' compounds were chemically and structurally related to elements of group IV should lead to similarities in their semiconducting behaviour. This should not only increase the number of semiconductors resembling germanium, but the modification of the bonding relationships should also be reflected in the semiconductor characteristics. Today, the 35 compounds are among the best known compound semiconductors.

The success of this approach gave impetus to a further systematic examination of examples of the tetrahedral structure outside the Grimm-Sommerfeld compounds [3–5]. E. Parthé showed that all theoretical cases can be covered by means of an extension of the Grimm-Sommerfeld rule. The first consequence is that for binary compounds, bonds between like atoms are also allowed. For a compound of composition Q_nR_m . . . the generalized form of the Grimm-Sommerfeld rule, as given by Parthé, states that:

$$\frac{ne_q + me_r + \ldots}{n + m + \ldots} = 4$$

where e_q, e_r . . . represent the number of valence electrons of atoms Q, R, . . . In the case of binary compounds, all possible combinations can be obtained, if e_q has values between 1 and 4, and e_r values from 4 to 7: the values of n and m that satisfy the equation may thus be determined. This yields, as can easily be confirmed, ten different combinations:

$$e_{q_n}e_{r_m} \equiv 44,\ 35,\ 26,\ 17,\ 3_26,\ 3_37,\ 25_2,\ 2_37_2,\ 15_3,\ 1_26_3$$

The first four cases comprise the Grimm-Sommerfeld compounds. Combination 25_2 corresponds to a compound such as ZnP_2 (figure 10). Compounds with more elements may be obtained by addition of these combinations, as is shown in the following example:

$$1_26_3 + 3_26 = 1_23_26_4 \equiv 136_2$$
$$\text{and} \quad 1_26_3 + 26 + 4 = 1_2246_4$$

Compounds such as $CuFeS_2$ and Cu_2FeSnS_4, respectively, correspond to these. A valuable advantage of the method is that, by means of a simple modification of the general equation, 'defect structures' can also be handled. This means that structures are considered in which some of the apices of the tetrahedron of atoms are unoccupied (figure 11).

Not all the compounds derived in the above manner can be synthesized, nor will they all have a tetrahedral structure. The special value of the method, however, is that all cases that are possible in principle are covered. Over 200 compounds with just this type of structure are now known, whereas in 1955 a table of all known

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semiconducting compounds listed only 100 substances [6]. The application of the rule is limited by the fact that not all elements in the Periodic Table can participate in a tetrahedral structure. The following section explains why the majority of the members of the class of compounds defined by the extended rule are semiconductors.

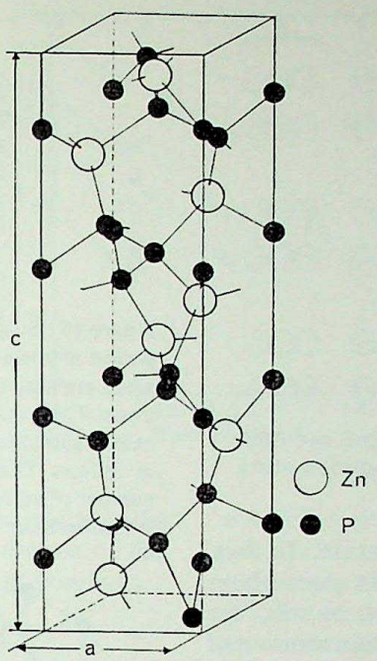

Figure 10 Structure of red ZnP_2. Deviation from the atomic ratio 1 : 1 leads to bonds between like atoms. [3]

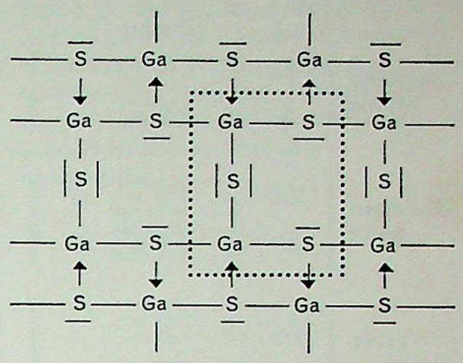

Figure 11 γ-Ga_2S_3 as an example of a defect structure. The ordered vacancies take on the role of atoms with zero valence electrons. They are surrounded tetrahedrally by the free electron pairs of the sulphur atoms. [3]

Principle of filled valence electron shells

Semiconductors generally have a filled valence-electron shell, and the rule that compounds with tetrahedral structure are generally semiconductors is based on the hypothesis that such a structure achieves this.

The situation in the semiconductor elements of group IV is relatively simple. Here we are dealing with more or less pure covalent bonding, and the filled octet is realized by each atom forming an electron-pair bond with four neighbouring atoms. The principle of shared electron pairs is found to apply for most elements that are 1 to 4 positions before an inert gas in the Periodic Table. The number of required electron pairs, and thus the number of nearest neighbours in the structure, is $\mathcal{N}-8$, where $\mathcal{N}$ is the group number. The tendency to fill up the electron shells is also present when these elements are partners in compounds. E. Zintl, in his work in the thirties, pointed out the singular behaviour of these elements, and the expression *Zintlgrenze* (Zintl boundary) for the line that separates these elements from the others in the Periodic Table has become an accepted term (table IV). It turns out that, as a rule, we have a semiconductor when one component of a compound is a Zintl element with a filled eight-electron valence shell.

The electron shells can also be filled by electrons from a component of lower ionization energy; the bonding—

Table IV
Periodic Table of the elements. Elements which occur as members of tetrahedral structures are italicized [9]

Levels	Rare gases	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	VIII_A			I_B	II_B	III_B	IV_B	V_B	VI_B	VII_B	VIII_B
															Zintl elements				
	He	*Li*	*Be*											*B*	*C*	*N*	*O*	*F*	Ne
2s	0	1	2											2	2	2	2	2	2
2p														1	2	3	4	5	6
	Ne	Na	*Mg*											*Al*	*Si*	*P*	*S*	*Cl*	A
3s	0	1	2											2	2	2	2	2	2
3p														1	2	3	4	5	6
	A	K	Ca	Sc	Ti	*V*	Cr	*Mn*	*Fe*	Co	Ni	*Cu*	*Zn*	*Ga*	*Ge*	*As*	*Se*	*Br*	Kr
3d	0	0	0	1	2	3	5	5	6	7	8	10	10	10	10	10	10	10	10
4s	0	1	2	2	2	2	1	2	2	2	2	1	2	2	2	2	2	2	2
4p														1	2	3	4	5	6
	Kr	Rb	Sr	Y	Zr	Cb	*Mo*	Tc	Ru	Rh	Pd	*Ag*	*Cd*	*In*	*Sn*	*Sb*	*Te*	*I*	Xe
4d	0	0	0	1	2	4	5	6	7	8	10	10	10	10	10	10	10	10	10
5s	0	1	2	2	2	1	1	1	1	1	0	1	2	2	2	2	2	2	2
5p														1	2	3	4	5	6
	Xe	Cs	Ba	La	Hf	Ta	*W*	Re	Os	Ir	Pt	Au	*Hg*	*Tl*	Pb	*Bi*	*Po*	At	Rn
4f	0	0	0	0	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
5d	0	0	0	1	2	3	4	5	6	7	9	10	10	10	10	10	10	10	10
6s	0	1	2	2	2	2	2	2	2	2	1	1	2	2	2	2	2	2	2
6p														1	2	3	4	5	6
		M		T								B							

(H and 1s level are excluded.)

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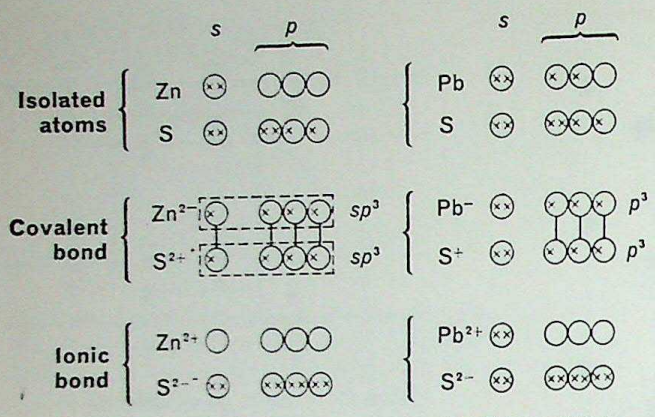

Figure 12 Covalent and ionic formulations for ZnS and PbS. The formal charges introduced do not allow prediction of the actual sign of the dipole of a bond. [9]

an ionic bond—is then electrostatic in nature. In fact, pure ionic bonding does not occur even in cases where there are large electronegativity differences, as, for example in CsF, but every bond has a certain amount of ionic bonding mixed with covalent bonding. However, it is possible in nearly all cases to use formally either an ionic or a covalent notation for any compound (figure 12). Ionic formulation has the advantage of simplicity, since the valency to be used in the formula of the compound is prescribed by the group requirement of the element to achieve a filled valence shell (table v). Even cases of semiconductors such as CsAu, in which no Zintl-element participates, can be included in this treatment (gold has about the same electronegativity as iodine).

The ionic formulation is helpful in finding new semiconductors. If one starts with an element or compound of known structure, one may replace one or more elements without disturbing the structure, provided the concentration of valence electrons is unaltered. The method is known as the 'substitution rule' [7], and it can be used in conjunction with the principle described above to extend the range of semiconductors (figures 13, 14): it is not limited to compounds with tetrahedral structure. This fact has considerable practical significance, since there are nowadays representatives of many types of structure among the semiconductors. Where the changes in the character of the bonding and in the ratio of the sizes of the substituting atoms are not too great, we can expect to find the properties of the parent substance reproduced in modified form in the derived compound. Thus, if the difference in electronegativities is made larger, that is, if there is an increase in the contribution from ionic bonding, this will lead in general to an increase in the forbidden-energy gap.

In recent years, E. Mooser and W. B. Pearson [14] have tried to extend the $N-8$ rule, referred to already, to a general valence rule including also non-tetrahedral compounds. In this way all semiconductors in which Zintl elements are present would be covered, irrespective

Table V

Examples of the ionic formulation of semiconducting compounds taken from Goodman [7]

$Zn^{2+}Se^{2-}$	$Mg_2^{2+}Sn^{4-}$	$Pb^{2+}S^{2-}$	$Fe^{2+}(S-S)^{2+}$
$Ga^{3+}As^{3-}$	$Li^{1+}Mg^{2+}Sb^{3-}$	$Bi_2^{3+}Te_3^{2-}$	$Cu_6^{1+}Fe_2^{2+}S_5^{2-}$
$Ag^{1+}In^{3+}Te_2^{2-}$	$Ag_2^{1+}Te^{2-}$	$(Cd,Cd)^{4+}(Sb-Sb)^{4-}$	
$Zn^{2+}Ge^{4+}As_2^{3-}$	$Cu_2^{1+}O^{2-}$	$Na^{1+}Au^{1-}$	$Mg_3^{2+}Sb_2^{3-}$

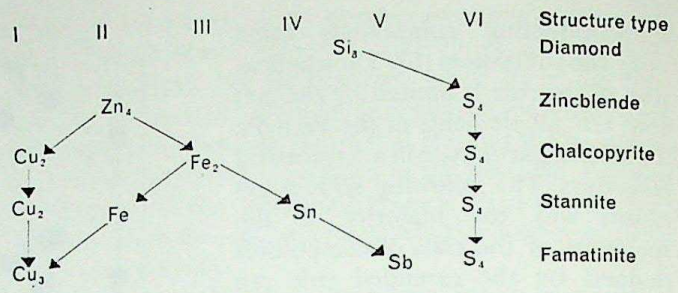

Figure 13 Substitution rule. Starting with an element or compound of known structure one or more elements are replaced while maintaining a constant concentration of valence electrons. The exchange can take place either on the anion or cation sublattice. The Zintl-elements can act either as anions or cations. The concentration of valence electrons is 4. The number of valence electrons corresponds to the group number in the Periodic Table. [3]

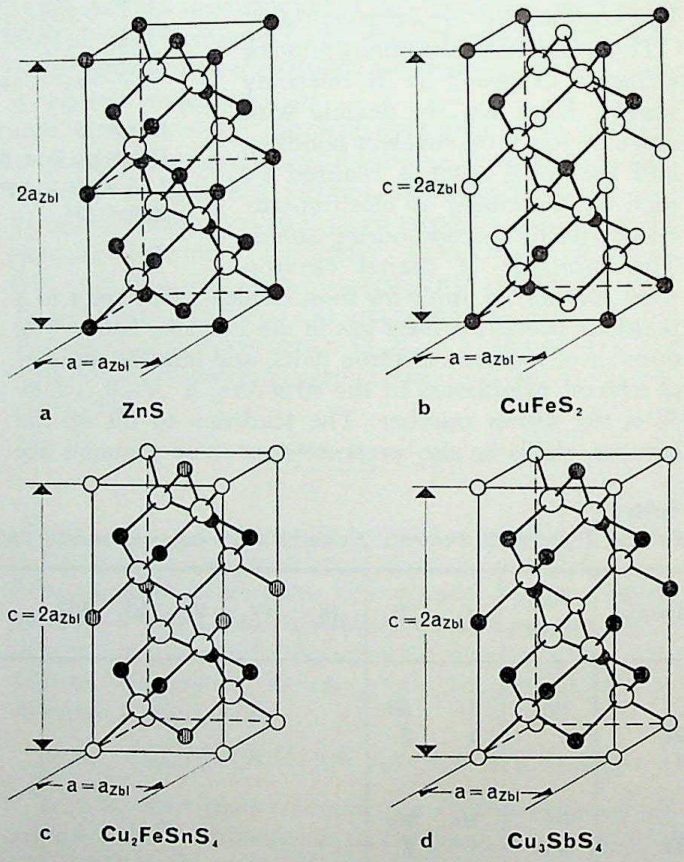

Figure 14 Superstructures of zincblende type. The structures of figure 13a are derived from the zincblende structure (a) by the ordered distribution of metal atoms in the equivalent points of zinc. (b) chalcopyrite, (c) stannite, (d) famatinite. (○ Fe Sb ◍ Sn ● Cu Zn ◯ S)

of the kinds of valence-hybridization existing. This formulation, initially too simple, has been extended over the years to cover structures in which cation-cation or anion-anion bonds occur, and likewise cases where not all the valance electrons are assigned to bonds, but exist instead as free valence electron pairs.

The rule, in its extended form, states that

$$(n_e+b_a+b_c)/n_a=8$$

Here n_e is the total number of valence electrons; b_a is the number of electrons assigned to anion-anion bonds; b_c the number of electrons assigned to cation-cation

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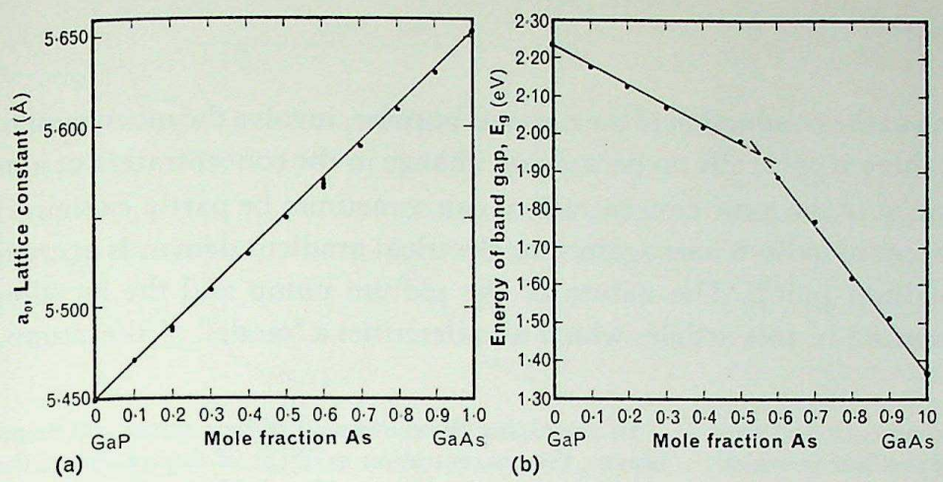

Figure 15 $GaP_{(1-x)}As_x$ solid solutions [17]. (a) Lattice constants as a function of composition. (b) Energy gap as a function of composition. The observed discontinuity is caused by a difference in band structure of the two components.

bonds and to free electron pairs, or to either; and n_a is the total number of anions. Ignoring details, the use of this rule is exemplified by ZnP_2 for anion-anion bonding:

$$ZnP_2: n_e = 12, n_a = 2, b_a = 4, \text{ and } b_c = 0$$

This rule, which at first sight appears attractive, has been the object of much criticism. The main practical objection is the difficulty of defining the necessary parameters, especially in complicated cases. It is to the credit of the authors, however, that they have established the existence of general ideas underlying all semiconductors, and their concepts suggest the direction in which a final solution of the problem might lie [8–11].

Compounds of the transition metals

The concepts outlined above are limited to compounds of the elements of the main groups in the Periodic Table, and are applicable only in exceptional cases for compounds involving transition elements. Transition elements are characterized by the ease with which they undergo valency change, and by the tendency to form wide non-stoichiometric phase regions: for compounds of such elements the application of band models appears to offer only limited possibilities. Moreover, in only a few cases has it been possible to produce single crystals of such compounds that are comparable in purity and perfection with those obtained with some 35 compounds. As a result, all attempts so far to extend the concepts developed above to this class of compounds have failed. These substances are, however, of great importance in the electronic industry as resistors, dielectrics, and magnetic materials.

Mixed crystals

Mixed-crystal formation is often used for producing a continuous change of physical properties. In the simplest case, we are concerned with solid solutions of elements or of compounds of the same general formula belonging to the same lattice type (figure 15). The various atoms are distributed randomly over the particular lattice sites. A linear relationship is often observed between certain parameters; for instance, between the lattice constant and the composition.

It must be noted that mixed-crystal formation is not limited to compounds of the same lattice and formula type. Among the most important prerequisites for their formation are: (a) lattice elements of comparable size; and (b) a similarity in the character of bonding and polarizability. However it cannot always be predicted with any certainty whether two systems are completely miscible or not. This problem, very important in semiconductor research, needs intensive study.

It is difficult to grow homogeneous mixed crystals out of the melt, but crystal-growing from the gas phase, using gaseous reaction components, has proved rewarding [12]. The temperatures involved here are usually so low that diffusion in the condensed phases, critical in melt-growing of crystals, can be neglected. Such methods have therefore been utilized in the growing of mixed crystals [13].

Acknowledgement

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The sodium pump

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P. F. Baker

Many biochemical processes, such as the conduction of the nervous impulse, involve the movement of ions across a cell membrane, but there is generally no permanent change in the concentration of ions inside the cell. The re-establishment of the ionic concentrations can sometimes be partly explained electrochemically, but the movement of sodium ions against an electrical gradient demands energy. This process is known as the sodium pump. The nature of the sodium pump and the location of the enzymes involved are discussed in this article, which also describes a 'model' of the pump.

The composition of the internal environment of all animal cells differs markedly from that of the fluid in which the cells are immersed. This is very clear when one considers their respective contents of ions in free solution: the interior of the cell is rich in potassium ions and organic anions and poor in sodium and chloride ions, whereas the reverse is true of the bathing medium. The reason why these differences arose in evolution is not known, but they are now essential to the proper functioning of the body. To quote two examples: ion gradients play an important part in the transmission of the nervous impulse [1], and many intracellular enzymes require potassium as a cofactor [2].

The interior of the cell is separated from whatever surrounds it by a thin fatty membrane. This membrane, which is only about 100 Å thick, is thought to be the main barrier between the internal and external solutions, and has been attributed with considerable powers of discrimination between different ion species. A membrane of this type cannot explain the origins of the ionic disequilibrium, but once the ionic differences are set up, it would impede the subsequent re-mixing of the two solutions. The simplest way of maintaining the gradient would be to have a completely impermeable cell membrane; however, experiments with radioactive tracers have shown that the membrane allows all small ions to pass, although at varying rates. Thus the maintenance of steep ionic gradients cannot be ascribed to a totally impermeable membrane, and it is therefore necessary to assume that work is constantly being done to maintain them.

In excitable cells such as nerve and muscle, the generation of electrical signals involves the movement of ions down their concentration gradients, and in these tissues some means of resetting the gradients is essential if function is to be maintained. The necessity for such a system was realized as long ago as 1902 by the German physiologist E. Overton, who pointed out that human heart muscle made some $2{\cdot}4 \times 10^9$ contractions in 70 years; yet, so far as he knew, it contained just as much potassium, and as little sodium, in old age as in early youth. Although nerve and muscle have been favourite tissues for studying the mechanisms involved in producing and maintaining the ion gradients, similar mechanisms are found to varying extents in all cells, and red blood cells are another experimental material that has been much used.

P. F. Baker, *M.A., Ph.D.*

Was born in Lincoln in 1939 and educated at Lincoln School and at Emmanuel College, University of Cambridge. He is now a Demonstrator in Physiology and Official Fellow of Emmanuel College. His research interests include the mechanism of ion movements across cell membranes, and also the processes of fertilization and cell division.

In examining the movement of ions across cell membranes, the concentration gradient of the ion is not the only factor that must be considered. Most cell membranes are polarized—the interior of the cell is negative with respect to the outside—and this potential may help or hinder the movement of ions down their concentration gradients. Thus the negativity of the cell interior makes the uptake of potassium ions much easier than the adverse concentration gradient suggests: indeed, if the potential is large enough, potassium ions will be drawn passively into the cell against the chemical gradient. On the other hand, both the chemical and electrical gradients are opposed to the movement of sodium out of the cell, and energy must be used in this movement. The process by which it is achieved is known as the sodium pump.

Measurement of ion movements

Most of the early experiments on the sodium pump in excitable tissues were performed on the giant nerve cells of cephalopods, squid in particular. These cells are many centimetres long and up to a millimetre in diameter. The cell is readily dissected out of the animal and remains functional for many hours when kept immersed in sea water. The large size of these cells makes it possible to manipulate them in ways that are very difficult with other cells; one such technique is the injection of solutions into the cells. By injecting radioactive sodium ions into squid axons, P. C. Caldwell, A. L. Hodgkin, R. D. Keynes, and T. I. Shaw [3] were able to investigate the properties of the sodium pump in a single nerve fibre.

They first investigated the dependence of the extrusion of sodium ions on metabolism. Nerve is predominantly an aerobic tissue, and its energy reserves, which are in the form of the high-energy compounds adenosine triphosphate (ATP) and phosphagen, can be almost completely broken down by poisoning the nerves with cyanide, dinitrophenol, or azide. Application of any one of these poisons markedly reduced the efflux of radioactive sodium ions from squid axons, and the rate at which the efflux declined closely paralleled the fall in the amount of high-energy phosphates present. Removing the poison usually allowed resynthesis of the energy-rich phosphate compounds, and when this occurred a parallel increase in the sodium efflux was observed. If ATP or phosphagen was injected into a fully poisoned axon, but not if these compounds were placed in the external medium, there was a brief period of increased sodium efflux and the magnitude of this depended on the amount of ATP or phosphagen injected (figure 1). These experiments strongly suggest that energy-rich phosphate compounds are involved in the mechanism of sodium extrusion from squid axons.

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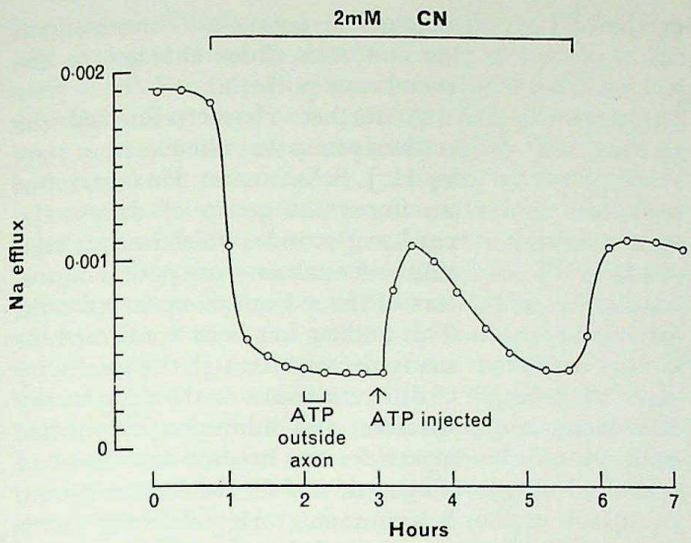

Figure 1 The effect of the respiratory poison, cyanide, on the sodium efflux from a squid axon. The figure is only diagrammatic and intended to show the kind of changes in efflux observed when ATP is returned either to the outside or the inside of a poisoned axon. The sodium efflux is expressed as the fraction of radioactive sodium (^{22}Na) lost per minute.

Similar evidence is available for the red blood cell. Mature human red blood cells obtain all their energy from glycolysis, and M. Maizels showed that inhibition of glycolysis with iodoacetic acid stopped the extrusion of sodium from these cells. The action of metabolic inhibitors suggests that energy-rich phosphate compounds are involved, but it is very difficult to decide which compounds are actually supplying the energy to the pump. This difficulty arises because of the presence of numerous enzyme systems in the cell, which ensure that energy supplied in one form will rapidly be converted into all the other forms present in the cell. G. Gardos developed an elegant method for minimizing these problems, which is based on a simple stratagem. If red cells are placed in a dilute medium, they swell: as they swell, their cell membranes become progressively more leaky, the result being a rapid exchange of substances between the cell and the bathing medium. Provided the process is not allowed to progress too far, the red cells, now known as 'ghosts', can be resealed by returning them to a normal medium. If the cells are made to swell in a large volume of fluid, the normal contents of the cell can be removed by dilution and replaced by the constituents of the bathing fluid. The resealing process allows these ghosts to be transferred to different media without loss of their new contents. It was soon found that ghosts would still pump sodium provided they contained sodium ions and ATP. Other phosphate compounds were poor substitutes for ATP, which suggests that, at least in red cells, ATP is the main source of energy for the sodium pump. The red cell is still the only cell for which clear evidence is available to show that the source of energy for the sodium pump is ATP.

In many tissues, it is not necessary to use radioactive isotopes to demonstrate the energy requirement of the sodium pump. It is often possible to measure a net increase in the internal sodium content following inhibition of metabolism, and a net loss on removing the inhibitor. This is particularly easy for tissues with a very large area of surface membrane. Good examples are slices of brain and kidney cortex, and the nerve trunks that run down the legs of crabs. This last tissue contains thousands of nerve fibres which are very different in size from squid axons. The nerve fibres are often only 10^{-3} mm in diameter, and it has been estimated that in 1 g of nerve, there is 10^4 cm^2 of nerve membrane. Such a tissue is ideal for studying the sodium pump, and it is very easy to show that a large net increase in internal sodium content follows the application of cyanide to these nerves. The observation that the sodium content rises when metabolism is inhibited is itself evidence for a constant leak of sodium into the nerve. As the sodium content of unpoisoned nerves immersed in sea water remains constant, it must be concluded that energy is constantly being used to keep pace with the inward leak of sodium.

So far I have described only evidence that shows that the extrusion of sodium from cells requires metabolic energy. What other properties does this mechanism have? When sodium leaks into a cell, it usually does so in exchange for the main internal cation, potassium, and a return to the original condition requires not only the extrusion of sodium from the cell but also the reabsorption of potassium. Both processes are inhibited by metabolic poisons and it is natural to enquire whether the process of sodium extrusion is in some way coupled to the uptake of potassium.

In both nerve fibres and red blood cells, the complete removal of potassium from the external medium markedly reduces the efflux of sodium; increasing the concentration of potassium in the medium increases the sodium efflux. In red cells, this dependence on external potassium was examined in some detail by I. M. Glynn [4] who showed that the curve relating energy-dependent sodium efflux to external potassium concentration approximated closely to a rectangular hyperbola. A relation of this kind is often seen in enzyme reactions and suggests that potassium ions might be activating sodium-ion extrusion by combining with some site on the outside of the cell membrane. Whether the potassium ions activating sodium extrusion are also the potassium ions taken up by the cell is not certain: it is still possible that there are quite separate sites for activation by potassium and for potassium transport.

It now seems likely that activation of the sodium pump by potassium is essentially similar in both nerve and red cells; but an alternative mechanism seemed, at first, attractive for nerve. The resting potential of the nerve membrane is in effect a potassium diffusion potential created by the tendency for potassium ions to diffuse out of the nerve down their concentration gradient. Removal of external potassium increases this gradient and so raises the potential, making the inside of the cell more negative. Hodgkin and Keynes wondered whether the increase in potential was in itself adequate to stop sodium extrusion. They tested this suggestion experimentally in the following way. Cuttlefish axons were charged with radioactive sodium ions and immersed in sea water containing a 10 mM concentration of potassium. The rate of sodium extrusion was measured first in sea water; then with the membrane potential increased by electrical means to a value close to that normally seen in potassium-free sea water; and finally without the electrical hyperpolarization. The sodium efflux remained constant throughout. This experiment suggests that the large changes in sodium efflux which result from small

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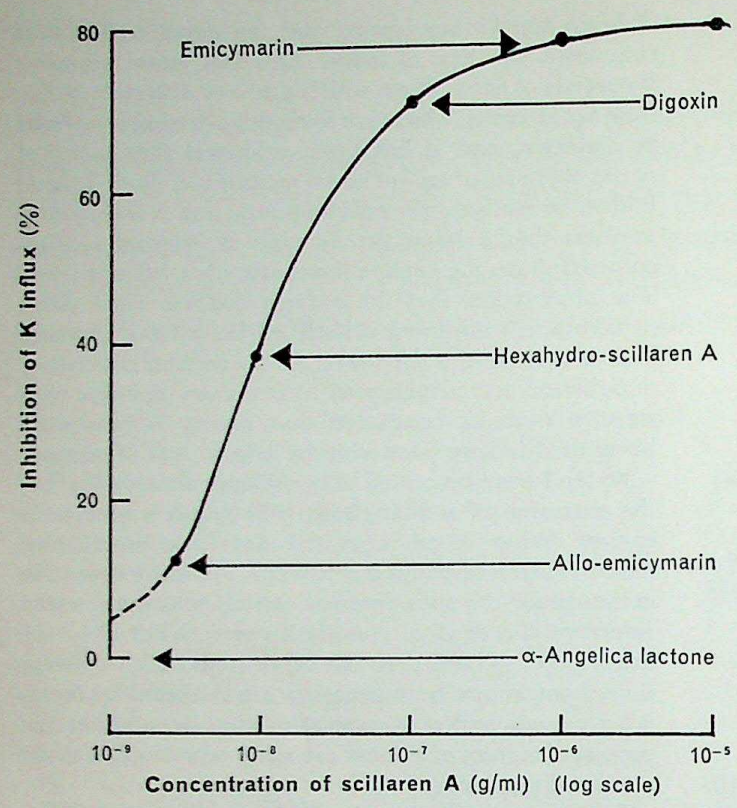

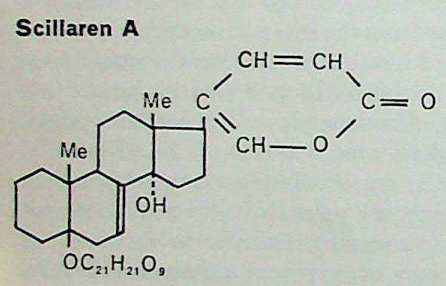

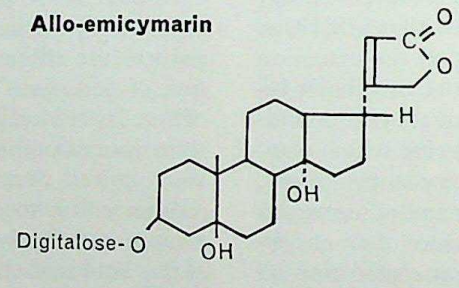

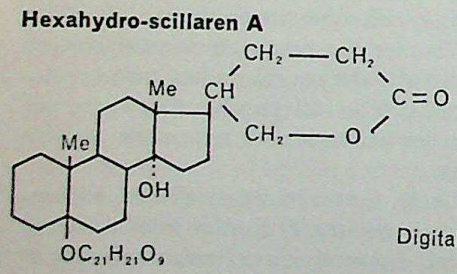

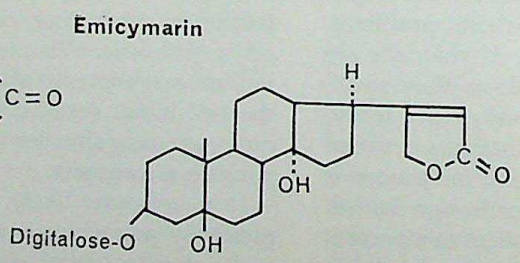

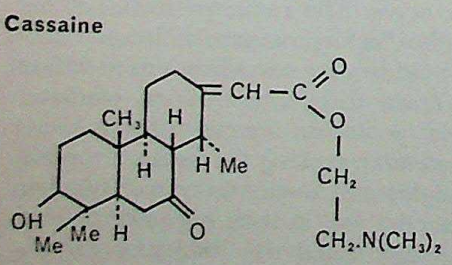

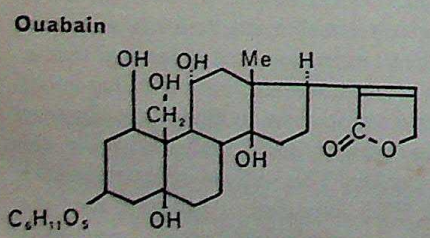

Figure 2 Graph showing percentage inhibition of K influx into red cells at different concentrations of the glycoside scillaren A. The arrows represent the percentage inhibition caused by 10^{-6} g/ml of the glycosides. Digoxin is similar to emicymarin. The formulae of ouabain and cassaine, both of which inhibit the pump, are also included. (After Glynn.)

changes in potassium concentration do not stem from changes in the membrane potential.

A further characteristic of the sodium pump was discovered in 1953 by H. J. Schatzmann. He found that an important group of drugs—the cardiac glycosides which include digitalis and ouabain—are potent inhibitors of the sodium pump in red cells. This finding has been confirmed for many tissues, although the sensitivity of different tissues to the drug is very variable, and inhibition by cardiac glycosides has become an important diagnostic tool for the sodium pump. Schatzmann's original observations were extended by Glynn, who examined a series of different glycosides to determine the chemical features necessary for inhibition (figure 2); and by Caldwell and Keynes, who showed that high concentrations of ouabain injected into a squid axon were ineffective in blocking the pump, whereas very low concentrations were effective when added to the external medium. This latter observation suggests that the site of action of ouabain is at the outside of the cell membrane, but it is possible that the injected ouabain had been inactivated in some way before it could reach the inner face of the cell membrane. Glynn also showed that as few as 1000 molecules of glycoside per red cell gave complete inhibition of the sodium pump. This suggests that the pumping sites are very thinly distributed over the cell surface.

In summary, these experiments on intact cells show that for sodium ions to be pumped out of cells both metabolic energy—probably in the form of ATP—and external potassium ions must be available, and that the process is inhibited by ouabain in the external medium.

Involvement of an enzyme system

ATP is usually handled in the cell by enzyme systems, and J. C. Skou [5] wondered whether an enzyme system with the properties of the sodium pump could be isolated from cells. When his first paper appeared in 1957 it constituted a major

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advance, and subsequent work has confirmed his findings and extended them to a wide variety of tissues. In his early work, Skou used crab nerve and isolated from it a membrane fraction which, in the presence of magnesium ions, was capable of hydrolysing ATP. The rate of hydrolysis was only slightly increased by the addition separately of either sodium or potassium ions; but when these ions were added together, the rate showed a large increase. Ouabain stopped this hydrolysis. These observations were extended by R. L. Post and his co-workers, who showed that in red cells, the potassium-ion concentration required to achieve half the maximum rate of hydrolysis was very similar to that required for 'half-maximal' activation of the sodium pump in intact cells. In addition, Dunham and Glynn showed that the effectiveness of different glycosides in inhibiting the hydrolysis closely paralleled their action on the sodium pump.

Although these results strongly suggest that the enzyme hydrolysing the ATP is part of the sodium pump mechanism, it is still essential to show that the enzyme is present in the cell membrane, and that the sites of ATP breakdown and sodium activation are internal to the cell membrane and that the site of potassium activation is external.

Localization of the enzyme system

These tasks have now been achieved for both red cells and nerve fibres. Using red cell ghosts, I. M. Glynn, R. L. Post, and R. Whittam, working in separate laboratories, have all shown that with potassium and ATP inside the ghost, the rate of ouabain-sensitive hydrolysis of ATP is very low, whether or not sodium and potassium are present in the external medium. However, with sodium and ATP in the ghost, the rate of hydrolysis is high when potassium is included in the external medium and low when potassium is absent. The products of ATP hydrolysis—adenosine diphosphate (ADP) and orthophosphate—are not released into the medium surrounding the cell.

With nerve fibres, two main approaches have been employed. In experiments on intact nerve fibres, C. M. Connelly and the author [6, 7] have made use of the 'phosphate cycle' in cells (figure 3). The breakdown of ATP produces ADP and orthophosphate, and these in turn stimulate the processes by which ATP is resynthesized. As nerve is predominantly aerobic, the resynthesis of ATP is associated with an uptake of oxygen. An increase in the rate of ATP utilization will increase the levels of ADP and orthophosphate in the cell, and these in turn will increase the rate of consumption of oxygen. A decrease in the rate of ATP hydrolysis will have the opposite effect: a fall in ADP and orthophosphate, and a reduction in the rate of consumption of oxygen. Thus by measuring both the rate of oxygen uptake and the orthophosphate content of crab nerve, it is possible to follow changes in the rate of energy utilization. With this technique, it can be shown that inhibition of the sodium pump, either by removing external potassium or by adding ouabain, produces a fall in the orthophosphate content of the cell and a reduction in consumption of oxygen. Experiments of this kind indicate that in crab nerve, 50–75 per cent of the resting metabolic energy of the cell is used in pumping out sodium.

A convenient feature of nerves is that the conduction of action potentials following electrical stimulation causes

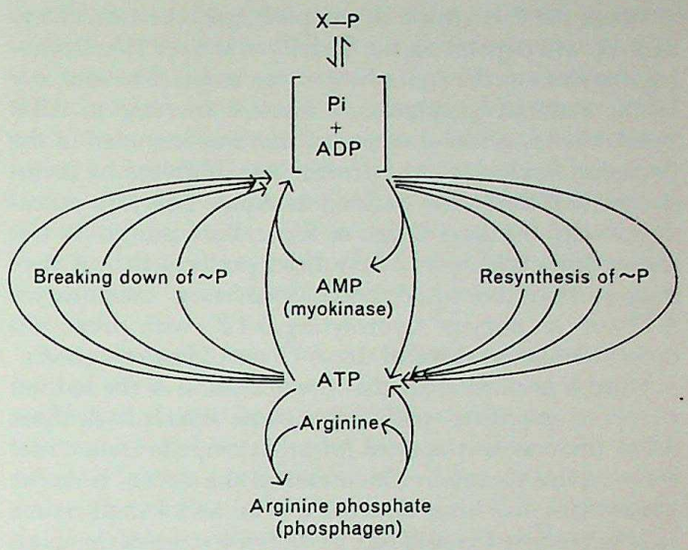

Figure 3 The phosphate cycle in cells. As a cell is a closed system, in the absence of an external source of orthophosphate (P_i) the intracellular level of P_i must depend on the relative rates of synthesis and breakdown of phosphate compounds. The scheme shows the major reactions involved. In squid and crab nerve the phosphagen is arginine phosphate; but this is replaced by creatine phosphate in mammals. X-P represents phosphate in combination with other organic molecules, for example, sugars.

them to gain sodium and lose potassium. Stimulation also elevates the orthophosphate level and increases the rate of oxygen consumption, and both these effects are reduced or abolished if the external medium lacks potassium or contains ouabain. These experiments suggest that the increase in energy utilization requires either a rise in the internal sodium content or a fall in that of internal potassium, together with the presence of potassium in the external medium. The crucial question is to decide whether it is the rise in internal sodium or the fall in internal potassium that acts as a trigger for the observed changes. Nerves continue to carry impulses when immersed in solutions in which the sodium has been replaced by lithium and, under these conditions, the nerves gain lithium and lose potassium: lithium gained in this way appears not to be pumped out of the nerve. Stimulation of crab nerves in sea water in which the sodium has been replaced by lithium, and which contains potassium, does not elevate the orthophosphate level, nor does it increase the oxygen consumption. It might be argued that lithium is inhibiting the pump; but if the stimulation is performed in a mixture of sodium and lithium, the normal changes are seen. These experiments indicate that it is the rise in internal sodium and not the fall in internal potassium which triggers the changes in metabolism.

Recently, a more direct method for studying the energy utilization of the sodium pump in nerve has been devised by T. I. Shaw and the author. It makes use of the 'perfused' axon [1]. It is possible to squeeze the protoplasmic contents out of a squid giant axon—rather in the way one squeezes toothpaste out of a tube—and refill the flattened sheath with a solution of known chemical composition. Despite this rather brutal treatment, the nerve membrane is left behind in a fairly undamaged condition, and provided the perfusion medium is rich in potassium ions and has the same osmotic pressure and pH as sea water has, the perfused axon will conduct nervous impulses.

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When ATP is added to the perfusate, the rate of hydrolysis will depend on the activity of the ATP-hydrolysing enzymes at the inner face of the membrane and any in the residual axoplasm. A marked increase in ATP breakdown was found when sodium was included in the perfusion fluid, and this increase was inhibited by inclusion of ouabain in the bathing medium. This is in accordance with our knowledge of the sodium pump. So far, rather few experiments have been performed; but they suggest that the squid nerve membrane contains an ATPase (an enzyme hydrolysing ATP) with properties rather similar to those of the ATPase of red cell ghosts.

Once it became clear that the operation of the sodium pump is associated with an enzyme which hydrolyses ATP, the way was opened for an attempt to isolate and characterize the molecules of which the system is made. Much work has been directed to this, and I shall return to it later: first I would like to describe some of the more detailed properties of the pumping mechanism in intact cells. These studies are of great importance, because the pump usually operates with different solutions on the two sides of the membrane: once the cell is broken and the membrane isolated, this difference is lost. It is quite possible that some essential features of the pump are lost during isolation of the ATPase—for instance, no one knows whether or not the isolated ATPase can actually move ions across the membrane fragments in which it is located.

Stoichiometry of the sodium pump

One question is of considerable interest: how many sodium and potassium ions are moved for each energy-rich phosphate bond that is broken? Does the pump have a fixed stoichiometry, or can it vary the number of sodium ions carried, in response to the steepness of the electrochemical gradient? Experiments on both red cells and nerve have shown that for each energy-rich phosphate bond split, some two to four sodium ions are pumped out of the cell, in exchange for rather fewer potassium ions. The steepness and direction of the electrochemical gradient has no detectable effect on these values; but the electrochemical gradient was not made steeper in the experiments than the gradient that is normally encountered physiologically.

The fact that rather fewer potassium ions are reabsorbed than sodium ions extruded is interesting because it suggests that, unless some other ion is moved to maintain electroneutrality, the pump ought to be electrogenic —that is, capable of generating a potential difference across the membrane.

This potential difference has been searched for many times; but has been clearly shown in only a few tissues. The problem is that the resting potential of most cells is governed by the potassium-ion gradient, and a very active sodium pump might reabsorb potassium so fast that it increases the resting potential by lowering the concentration of potassium ions in the medium immediately external to the cell membrane. The only clear way of avoiding this problem is to show that, during pumping, the potential can rise above the value normally recorded when the resting cell is immersed in a potassium-free medium. An effect of this kind has been demonstrated in snail ganglia by G. A. Kerkut and R. C. Thomas [8]. They observed that injecting sodium acetate into the cells produced a large hyperpolarization, and that this was reduced by removing external potassium or by adding ouabain to the medium. These experiments show that the potential can rise above the 'zero potassium potential'; but they also show that external potassium is required for this to occur.

Skeletal muscle is another tissue in which there is good evidence for an electrogenic action of the sodium pump. In this tissue, it seems that at least part of the potassium uptake occurs passively, following hyperpolarization of the membrane by the sodium pump. This was first shown by R. P. Kernan and is clearly demonstrated in some recent experiments of R. H. Adrian and C. L. Slayman. The resistance of muscle cell membranes to the inward movement of rubidium ions is very much greater than the resistance to the inward movement of potassium ions: yet despite this difference in passive permeability, the rate of uptake of rubidium and potassium by the sodium pump is identical. (In activating the sodium pump, potassium ions can be replaced, to varying extents, by a number of other ions—for example, those of rubidium, caesium, ammonium, or thallium; but no substitute has been found for sodium ions.) Adrian and Slayman argued that if the pump exchanged sodium for rubidium or potassium on a one for one basis, there should be no marked difference in potential during pumping; but if part of the ion uptake occurs as a result of a hyperpolarization, then in order to achieve an equal rate of uptake of rubidium and potassium, the hyperpolarization must be much larger during rubidium absorption. When they did the experiment, they found a larger hyperpolarization during rubidium absorption. This supports the view that part of the uptake of potassium and rubidium is by a passive process coupled to the operation of the sodium pump through an increase in potential.

These experiments show that, in some tissues, the sodium pump is electrogenic. However, from the physiological point of view, the mechanism by which the hyperpolarization is achieved is not as important as the increased potential difference itself. Is there any evidence that such hyperpolarizations play any role in the body? It has been suggested that they may act as 'self-biasing' devices in the central nervous system—a period of high activity might give rise to a period of increased membrane potential and reduced excitability; but there is no clear evidence for this. There is, however, clear evidence for a role of the sodium pump in controlling the excitability of some smooth muscles. One of the many actions of the hormone adrenaline is to cause inhibition of contractions in the smooth muscle cells which surround the gut. E. Bülbring and her colleagues have shown that adrenaline causes a hyperpolarization of the membrane in isolated strips of muscle, and this effect is not seen in the absence of glucose (a source of energy); in media in which sodium is replaced by lithium; or in the presence of ouabain. Thus it seems that the hyperpolarization in this tissue results from an increased activity of the sodium pump.

Other modes of operation of the sodium pump

Although the sodium pump may move more sodium ions outwards across the cell membrane than potassium ions inwards, external potassium ions have been necessary in all the cases given so far. However, there are at least two other modes of operation of the sodium pump which do

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not require potassium in the external medium—in fact they occur only in the absence of external potassium. These are exchange diffusion of sodium, in which internal sodium is exchanged for external sodium; and the loss of sodium accompanied by an anion.

There is some evidence for the occurrence of exchange diffusion in nerve fibres; but the clearest evidence comes from the recent work of P. J. Garrahan and I. M. Glynn [9] on red cells. When red cell ghosts are filled with sodium and ATP and immersed in potassium-free media, there is no appreciable ouabain-sensitive loss of radioactive sodium; but when the experiment is repeated with a low concentration of sodium in the cells, or with a high intracellular sodium content together with a high level of orthophosphate, there is an appreciable sodium efflux. This efflux is much reduced by removing sodium from the external medium. Under conditions where there is an ouabain-sensitive efflux of sodium there is also an equal and opposite ouabain-sensitive influx of sodium. Thus it seems that internal sodium exchanges with external sodium by an ouabain-sensitive route without causing any net loss of sodium from the cell. Further experiments have shown that this exchange process requires ATP, but does not cause any appreciable ATP hydrolysis. Addition of potassium to the external medium abolishes the exchange, and energy is now needed to effect the extrusion of sodium coupled to the uptake of potassium. These observations raise a number of interesting questions, such as why the exchange diffusion is reduced by raising the sodium concentration inside the cell. However, from the point of view of the present discussion, the crucial observation is that sodium can be moved across the cell membrane by an energy-dependent and ouabain-sensitive route in the absence of external potassium.

The loss of sodium ions accompanied by anions has, so far, been seen only in nerve. In their early experiments on cuttlefish axons, Hodgkin and Keynes found an energy-dependent efflux of sodium into solutions that lacked both sodium and potassium ions. In more recent experiments on crab nerve, the author has shown [10] that there is an energy-dependent and ouabain-sensitive loss of sodium from nerves immersed in solutions free from sodium and potassium where osmotic pressure is maintained by choline or sugar. Under these conditions sodium ions are moving down the electrochemical gradient; but it still requires energy, and about three sodium ions are lost for each phosphate bond split. The loss of sodium is accompanied by an efflux of anions from the cell. A number of different anions are involved including glutamate, aspartate, and phosphate, the three major anions in crab nerve. Addition of potassium to the external medium cuts off the anion efflux without much affecting that of sodium; external sodium abolishes both the net loss of sodium and the anion efflux. These experiments indicate that in the absence of external sodium ions, external potassium ions are not essential for the movement of sodium across the nerve cell membrane. It is still not clear whether the anions actually form part of the mechanism of the sodium pump, or whether they are driven out of the nerve passively as a result of a marked increase in resting potential.

Chemical studies on the isolated ATPase

So far, we have considered mainly the properties of the sodium pump in intact membranes. I would now like to describe some of the recent work which has been directed towards an understanding of the chemical properties of the isolated ATPase preparation. In a number of laboratories, workers have tried to purify the ATPase to determine what molecules are necessary for the preparation to be activated by sodium and potassium. They soon found that any maltreatment of the membrane fragments in which the ATPase occurs caused loss of the enzyme that is activated by these ions. This observation suggests that some measure of structural organization is essential.

A more hopeful line has been the attempt to label some part of the ATPase system while it is functioning normally, and then to isolate and characterize the groups to which the label has become attached. The main technique so far has been the use of ATP containing radioactive phosphorus ($AT^{32}P$). When the ATPase preparation is treated with $AT^{32}P$, the amount of labelling is dependent on the ionic composition of the medium. The most exhaustive study of this has been made by R. L. Post, A. K. Sen, and A. S. Rosenthal [11]. They have shown that the labelling is low in the presence of magnesium ions alone, but is markedly increased on the addition of sodium ions. The inclusion of sodium and potassium ions in the medium results in a large reduction in labelling over that seen with sodium ions alone. This reduction is counteracted by adding ouabain to the medium.

These results can be interpreted in terms of alternate phosphorylation and dephosphorylation of the membrane during pumping. The phosphorylation requires sodium; and addition of potassium favours dephosphorylation by a mechanism which is blocked by ouabain. The immediate question is, to what kind of molecule is the ^{32}P attached? All the evidence points to combination with some sort of protein molecule rather than with one of the fatty constituents of the cell membrane. The phosphate appears to be combined as an acyl phosphate; but no one has isolated and characterized the molecules involved. Even when this has been done, it will be necessary to show that the labelled molecule really forms part of the pump mechanism and is not merely produced as an artifact of the isolation procedure. Such a step will be a great advance; but it will still be a long way to the ultimate goal of being able to explain the mechanism of operation of the sodium pump in chemical terms.

Models of the sodium pump

Many hypothetical models have been put forward to explain some or all of the properties of the sodium pump [12]; but, at present, all these models are little more than imaginative ideas. As yet, no experiments can distinguish clearly between them, and the only value of the models is that they provide a framework upon which to base future experiments that might lead to a deeper understanding. The models are all based on some form of shuttle or carrier molecule that can carry ions across the membrane. Some favour the view that a relatively small molecule might form a complex with the ion and then pass across the membrane: others prefer the concept of a large protein molecule that can change its shape, so that a site originally facing the internal solution can be brought into contact with the external one.

Despite the dangers inherent in thinking too much in terms of models, it is helpful to enquire whether any

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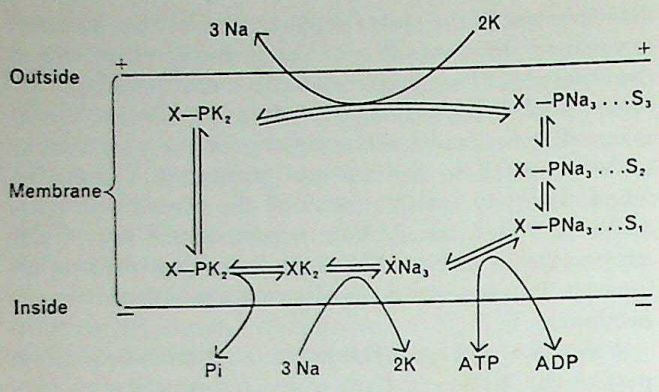

Figure 4 A hypothetical model of the sodium pump. It is based on the idea that the affinity for sodium and potassium ions of a cycling carrier is modified by combination with phosphate.

single model can incorporate all the major properties of the sodium pump. I would like to conclude by describing one such model. This model may not be much nearer the truth than any other; but it serves to draw together the various features of the pump mechanism. It is illustrated in figure 4. To explain the high affinity for sodium inside the cell and for potassium outside, it is assumed that metabolic energy is used to convert a carrier that already has a high affinity for sodium ions, and is 'loaded' with sodium, into a carrier with a high affinity for potassium. If this molecule is passed to a site within the membrane, the exchange of sodium on the carrier with internal potassium might be avoided. According to this scheme, the exchange of internal sodium with external sodium must occur through alternate breakdown and resynthesis of ATP. At the outer face of the membrane, if potassium is present, the carrier will react with potassium and return to the inside of the cell, where it is dephosphorylated and the potassium exchanged for sodium. If external potassium is absent, and if sodium is available, external sodium will tend to exchange with sodium on the carrier before the carrier returns to the inside of the cell. In the total absence of external potassium and sodium, sodium might dissociate from the carrier and the free carrier return to the inside.

The properties of exchange diffusion can be explained if the carrier has to cross the membrane by means of a series of sites (S_1, S_2, S_3). For exchange diffusion to occur, it must be possible for a carrier to pass freely from one side of the membrane to the other through these sites. If more than one site is occupied, and if exchange of sodium between carriers is impossible, exchange diffusion will be much reduced. Garrahan and Glynn found that exchange diffusion was lowest with high internal sodium concentrations and high ratios of ATP to ADP and orthophosphate, and these should both favour the formation of carriers that would occupy the sites across the membrane. During coupled pumping, reaction with external potassium presumably allows the carrier to return by a different route. The mode of action of ouabain remains obscure; but in the scheme shown in figure 4, combination of ouabain with site S_3 would block coupled pumping, exchange diffusion, and loss of sodium accompanied by an anion. The electrogenic properties of the sodium pump might be explained if sodium passes outwards as a positively-charged complex, and potassium returns in a neutral form.

This scheme is entirely speculative; but it will probably be many years before a detailed chemical description can be given. In the meantime, much has still to be learned about the physiological role of the sodium pump. One such problem is the transport of sodium and chloride across epithelia. The only method by which the body can increase its sodium content is to absorb sodium from the gut, often against an adverse electrochemical gradient. (Absorption of sodium also occurs in other tissues, such as the kidney and salivary gland, but here the body is merely conserving sodium ions that have leaked from the extracellular fluid.) In all these cases, sodium has to be moved across a layer of cells—in other words, unless it passes between the cells, and there is no evidence for this, it must cross two cell-membranes. There is evidence to suggest that in some tissues this is achieved by having, on the side from which sodium is to be absorbed, a membrane permeable to sodium and chloride ions; and on the other side, a membrane in which a powerful sodium pump is located. According to this view, sodium tends to diffuse into the cell at one side and is then pumped out at the other, chloride being drawn along passively. A spatial arrangement of this kind is attractive, but is still not fully proved. Another line of investigation stems from recent experiments that suggest that the sodium pump is involved not only in the movement of sodium and potassium ions across membranes, but also in the transport of organic molecules such as sugars and amino acids.

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NEUTRON SCATTERING

Thermal Neutron Scattering, *edited by P. A. Egelstaff. Pp. xv+523. Academic Press, London. 1965. 115s.*

This is not a book for the general reader, but it is ideal for the researcher who is considering the application of neutron-scattering methods to some problems concerned with the condensed state, either solids or liquids. It shows clearly how wide is the field of application. As the editor makes clear in his preface, the book is concerned with inelastic neutron-scattering processes only, and is to be regarded as a condensation of the original literature and a guide to it. There are ten chapters, written singly or jointly by fourteen contributors.

A chapter on introductory theory, incorporating 159 leading equations, is succeeded by three essentially experimental chapters, covering respectively mechanical and time-of-flight techniques, crystal diffraction techniques, and neutron sources and detectors. These are followed by reviews of the current position in the various branches of application: lattice vibrations, magnetic scattering, the structure of liquids, and the structure of molecules. As a typical example of the coverage we can mention Dolling and Woods' excellent review of thermal vibrations of crystal lattices. This is accompanied by a list of 165 references, 121 of which relate to work published in the 1960s, emphasizing the point that these inelastic scattering techniques have become valuable only since high-intensity reactor sources have become more widespread.

The editor has succeeded in achieving praiseworthy coherence among the chapters from his different authors, and the book is thoroughly recommended.

G. E. Bacon

COLLISION THEORY

The Theory of Atomic Collisions, *by N. F. Mott and H. S. W. Massey. (Third edition.) Pp. xxii+858. Clarendon Press, Oxford; Oxford University Press, London. 1965. 120s.*

Following the advent of quantum mechanics in 1925–26, the theory of scattering of electrons by atoms, or of atoms by atoms, made remarkably rapid progress, culminating in the publication of the first edition of this work in 1933. It at once achieved an ascendancy that may be measured by the fact that some thirty years elapsed before another book appeared on the same topic, which is central to modern physics. Since the second edition, in 1948, which included a discussion of nuclear collisions, the increasing understanding of plasma, and of atmospheric and nuclear physics have led to many important advances in both collision theory and its application. The recording of this new material, resulting in a doubling in size of the new edition, must have presented the authors with many problems, which have been overcome triumphantly so as to preserve entirely the style and flavour of the original work.

A full account is given of the basic theory of scattering of particles by a potential, including the recent investigations of the analytic properties of the scattering amplitude as a function of energy and momentum transfer. This is followed by an extension of the theory to many-body systems and its application to a wide range of atomic and nuclear phenomena. This volume will be indispensable for all those working in atomic and nuclear physics for many years to come.

B. H. Bransden

INORGANIC CHEMISTRY

Inorganic Chemistry, *Vols. I and II, by C. S. G. Phillips and R. J. P. Williams. Pp. xiii+685; x+683. Clarendon Press, Oxford; Oxford University Press, London. 1965; 1966. 65s. each.*

In this book, the authors have successfully developed the new approach to the subject by concentrating throughout on comparative chemistry, against a background of the relevant principles. The latter are discussed in detail in Part I of Volume I under the headings: wave mechanics, atomic structure and the Periodic Table, assemblies of like atoms, the bond model, the ionic model, the band model, equilibria, solid structures, electrode potentials, and kinetics and mechanism. In this section a large amount of factual information is brought together and correlated. In Part II of Volume I, the chemistry of the non-metals is reviewed on the basis of what has gone before. There is virtually nothing about experimental aspects of the subject, nor are certain important groups of compounds, such as the boron hydrides, treated in any detail. This shortcoming is, however, made good by a full bibliography at the end of each chapter listing review articles and other suitable sources.

Volume II deals with the metals, with special reference to their solid-state and solution chemistry and to the applications of modern valency theory to their compounds. The approach contrasts sharply with that in many other textbooks, especially in the relatively small amount of detail given and the way in which theoretical principles are emphasized. This is not an easy book to read, nor, in the reviewer's opinion, is it a comprehensive account of inorganic chemistry at the advanced undergraduate level, as the authors claim. There is much more to the subject than appears here. Nevertheless, it will be exceedingly valuable both to undergraduates and to those who lecture to them. A series of stimulating problems is included at the end of each chapter. The production is first class in every respect.

H. J. Emeléus

ANALYTICAL CHEMISTRY

Treatise on Analytical Chemistry, *Part I,* Theory and Practice, *Vol. 6, edited by I. M. Kolthoff and Philip J. Elving. Pp. xxiii+3347–4246. John Wiley & Sons, London. 1965. 175s.*

This volume maintains the high reputation of the comprehensive treatise on analytical chemistry; it is concerned with optical methods of analysis. There are chapters on emission spectroscopy by Scribner and Margoshes; flame photometry by Vallee and Thiers; infra-red spectroscopy by L. A. Smith; Raman spectroscopy by Rosenbaum; electron diffraction and scattering by Reisner; neutron absorption and scattering by Leddicotte; refractometry and dispersometry by Lewin and Bauer; optical rotation by Struck and Olson; chemical microscopy by McCrane and McCrane; and electron microscopy by Cocks.

Most of the chapters are good, up to date accounts of the various subjects—those on optical rotation, polarimetry, and chemical microscopy are probably the best. Modern apparatus is described and illustrated for many of the techniques but, surprisingly, no diagrams are given of commercial grating spectrographs, microphotometers, refractometers, flame photometers or chemical microscopes. Some of the diagrams, such as those on pp 3584 and 3600, are hardly appropriate for an advanced work, and atomic absorption spectroscopy receives very little attention. The table of atomic increments of refraction on p 3922 is not based upon recent experimental data, as the superior bond refractions are not tabulated. It is strange that W. R. Brode's book 'Chemical Spectroscopy' is not mentioned under sources of information on emission spectroscopy. However, these are all relatively minor blemishes in an otherwise valuable work.

A. I. Vogel

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CHROMATOGRAPHY

Dynamics of Chromatography, *Part I, Principles and Theory, by J. Calvin Giddings. Pp. xii+323. Edward Arnold, London. 1965. 90s.*

This volume, the first in a promised trilogy covering all aspects of chromatography, represents an attempt to provide a coherent and unified account of chromatographic theory that will be of practical value to chromatographers. Those familiar with the mathematical complexities of the theory will appreciate the magnitude of the task the author has set himself.

The work is introduced by lengthy sections on the dynamics of zone spreading and non-equilibrium theory. The treatment is clear, but, even so, it is questionable whether many will easily follow the detailed arguments. This is no fault of the author, since it seems unlikely that the subject will ever be representable in really simple terms. The succeeding sections on flow dynamics, diffusion and kinetic phenomena, and the achievement of separation are more straightforward, being based on more familiar ideas; practitioners may find here much information of value without too great demand on their mathematical ability.

This volume certainly represents the best account of theory to date and if the present high standard is maintained, this series should be very successful indeed.

J. H. Purnell

RADIATION CHEMISTRY

Pulse Radiolysis, *Proceedings of the International Symposium held at Manchester, April 1965, edited by M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale. Pp. xii+319. Academic Press, London. 1965. 70s.*

Pulse radiolysis is to radiation chemistry what flash photolysis is to photochemistry. It involves the delivery to a system of a pulse of high-energy electrons in the MeV range lasting between 10 and 1000 nanoseconds, and the measurement before, during, and after this pulse of any absorption or emission spectra. The major difference between most photochemical reactions and all radiation chemical reactions is that in the latter, an electron is always detached from the molecules of the irradiated system, an event that rarely occurs in the former. Moreover, an electron, when solvated by a wide range of important liquids such as water and the alcohols, is known to have a characteristic absorption spectrum with a large extinction coefficient. Consequently, although both techniques can be used to identify free radicals and electronically excited molecules, and to investigate the rates and the mechanisms of their reactions, pulse radiolysis has the added advantage of permitting the chemistry of the electron in various media to be studied easily.

Since this distinction was first realised in 1962, there has been a rapid growth in the number of publications involving the use of pulse radiolysis, and the book under review is the record of the first symposium wholly devoted to this technique and its applications. Obviously, the book is essential to radiation chemists, but it can also be recommended as containing much of general chemical interest and importance. The reader can learn about the rates at which electrons decompose, for example water and the alcohols; react with one another; or reduce solutes so as to generate species of special interest, such as hyper-reduced ions, Cd^{+} for example, and about the subsequent reactions of the adducts. Likewise, he can discover in these pages much about simple free radicals, such as OH, and their ionization, and about molecular ions such as CO_2^-, O_2^-, and O_3^-. It would be a poor chemist who would not derive some pleasure and profit from this book.

F. S. Dainton

CATALYSIS

Catalytic Hydrogenation, Techniques and Applications in Organic Synthesis, *by Robert L. Augustine. Pp. xii+188. Edward Arnold, London. 1965. 72s. 6d.*

From the point of view of theory, the subject of the metal-catalysed hydrogenation of organic molecules in solution is a meeting point of uncertainties. However, the subject is one of considerable practical importance, and it is this aspect that this book is concerned with. The main chapters are on apparatus and techniques, catalysts and conditions, hydrogenation of functional groups, and hydrogenolysis. Apart from considering some of the variables involved, the author has extracted from the voluminous literature of synthetic organic chemistry many of the useful procedures that have been developed in recent years. He makes an interesting effort to single out the method that appears to be most generally suitable for the hydrogenation of each of the main functional groups encountered in organic molecules. The value, for certain types of reduction, of the less familiar catalysts, rhodium and ruthenium, is noticeable.

Molecular hydrogen is the only reducing agent considered. Some mention might have been made of related procedures, such as the palladium-catalysed transfer of hydrogen from hydrazine to nitro-compounds to give amines, and the zinc/copper/aqueous ethanol method for the reduction of acetylenes to *cis*-olefins, for these methods are sometimes preferable to those involving hydrogen. Nevertheless, this is a very useful book.

H. B. Henbest

OCEANOGRAPHY

Chemical Oceanography, *Vol. II, edited by J. P. Riley and G. Skirrow. Pp. xv+508. Academic Press, London. 1965. 115s.*

The first volume of this text contained a series of articles by specialists on various aspects of the solution chemistry of sea water. The second, and last volume, is mainly devoted to the chemical aspects of the solid phases in contact with sea water, and to the equilibria between these and the solution phase. The geochemical topics which are covered by authorities in each field, include conditions of sedimentation (P. H. Kuenen); elemental geochemistry of marine sediments (R. Chester); dynamical aspects of the geochemistry of marine sediments (K. K. Turekian); and the geochemical history of the oceans (G. D. Nicholls). More specialist marine geochemical topics covered include the formation of marine sedimentary iron ores (H. Borchert); carbonate precipitation and dissolution in the marine environment (P. E. Cloud); oceanic salt deposition and metamorphism (H. Borchert); and a review of the occurrence of radioactive nuclides in sea water, marine sediments, and marine organisms (J. D. Burton). Together, these articles provide a most useful compilation of data, together with critical reviews of many important topics in marine geochemistry. The ninth article in the volume is a very timely review by J. P. Riley of the problems and practice of the analysis of sea water. All the articles carry extensive bibliographies and the volume has an extensive author and subject index.

The work suffers somewhat from the lack of close integration of the various articles that is inevitable in multi-author texts, but both volumes of this series together provide a valuable and greatly needed advanced textbook and reference work for postgraduate students and research workers in marine chemistry.

C. P. Spencer

GEOLOGY

The Geology of Scotland, *edited by G. Y. Craig. Pp. xv+556. Oliver and Boyd, Edinburgh. 1965. 105s.*

This handsome volume is notable for the

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quality of publication and for the excellent standard of illustrations; maps and diagrams are clear and effectively drawn and the photographs are well chosen and reproduced. A coloured geological map forms a folder at the end and adds lustre to the production. With a different lay-out, however, it could have been produced on a larger scale without occupying more space.

The first chapter is a masterly essay by T. N. George on the historical geology of Scotland. The following thirteen chapters by various authors then treat the broad elements of Scottish geology, as far as possible in chronological sequence. The final section is a useful summary of economic geology, and the volume is concluded with an effective index.

The volume is thus a compilation, but unlike many such works it contrives to maintain a coherence of form and uniformity of treatment. This has been partly achieved by allowing certain authors to write more than one chapter, where the topics require a measure of integration. It has also no doubt been facilitated by the fact that the book has largely been written by members of the University of Edinburgh.

The chapters are of sufficient length for the clear exposition and development of each topic, and the adequate lists of up to date references make the volume a comprehensive source-book.

B. C. King

BIOPHYSICS

Nonequilibrium Thermodynamics in Biophysics, *by A. Katchalsky and Peter F. Curran. Pp. x+248. Harvard University Press, Cambridge, Mass.; Oxford University Press, London. 1965. 68s.*

Several books have been published in recent years on nonequilibrium thermodynamics. These have been concerned chiefly with the development of the theory at an advanced level, and have dealt only briefly with the applications of nonequilibrium thermodynamics to biological systems. This aspect of the subject is covered by this book, which is a development of a lecture course given by the authors to graduate students of biophysics at Harvard University.

The first five chapters give a brief, largely descriptive account of the laws and functions of classical thermodynamics. These chapters are clear and well written, but do require some previous knowledge of thermodynamics. In the next three chapters, the authors develop the basic ideas of nonequilibrium thermodynamics, such as the dissipation function, the phenomenological equations, and Onsager's Law. Here, the emphasis is on the physical basis of these ideas rather than on a detailed mathematical treatment. This section is followed by six chapters dealing with the application of nonequilibrium thermodynamics to various transport processes, including diffusion, ionic conductance, and the permeation of membranes by electrolytes and non-electrolytes. Of particular interest are the sections on the frictional model of interacting flows, and the chapter on the relations between chemical reactions and diffusion processes (that is, active transport and facilitated diffusion). The last two chapters contain discussions of the statistical basis of Onsager's Law and the principle of minimum entropy production.

The authors succeed in giving a clear, simple introduction to the application of nonequilibrium thermodynamics to biological systems, and provide a good list of references to the scattered literature (up to 1964) on the subject. Students of biophysics, and their teachers, should find the book useful and interesting.

J. F. Thain

FUNGI

The Fungi, an Advanced Treatise, *Vol. I,* The Fungal Cell, *edited by G. C. Ainsworth and A. S. Sussman. Pp. xvi+748. Academic Press, New York. 1965. 192s.*

This is the first volume of a three-volume work. The succeeding volumes will deal with the fungus organism, fungal populations, and taxonomy. The objectives are described as summarizing what is known about fungi, as fungi, and the work is intended as a reference book.

The general treatment and objectives are to be welcomed as a return to the biological treatment initiated a century ago by the father of mycology, de Bary. However, the editorial work is disappointing in two ways. Firstly, chapters have either not been fully co-ordinated, such as those on mitosis and meiosis, or else have been foreshortened. This is presumably because the volume deals only with the cell and not the organism, and such chapters lose much of their impact: examples are those on transport and effects of light. Secondly, the editorial policy concerning content is not clear. Some chapters, such as that on nitrogen metabolism, deal comprehensively with all fungi; others deal with but a single fungus; yet others, such as that on terminal oxidations, hardly deal with fungi at all, yeast excepted.

Individual contributions are variable, as might be expected. Some of them include quite trivial information, such as the constituents of media and nutrients; others are admirable. I commend, in particular, the chapters on cell walls, mitosis, TCA cycle, nitrogen utilization, translocation, integration of metabolism, cellular extension, and branching and growth rhythms. The final chapter on gene action is admirable but ranges well beyond the fungi. This is a useful book which could have been improved by better and more consistent editing.

J. H. Burnett

MARINE BIOLOGY

Advances in Marine Biology, *Vol. III, edited by Sir Frederick S. Russell. Pp. x+402. Academic Press, London. 1965. 84s.*

The first of the four reviews in this volume is by M. J. Wells, on learning in marine invertebrates. A good brief account is given of learning and shape discrimination in *Octopus* and their connection with brain structure. Then follows a more general review of learning, useful for anyone searching for experimental animals in this subject. In another review, the effect on marine organisms of hot water from power stations is examined by E. Naylor. Some physiological work is summarized, but too much account has been taken of ecological anecdotes. An account of the dispersion of heat from the effluent pipe might have been given.

The biology of economically important seaweeds is described by A. D. Boney, and extensive data on resources in many parts of the world are summarized in a few succinct tables. Seasonal changes in life history and in extractives are described in a systematic arrangement, which makes the review rather long (120 pp.). There follow sections on use and harvesting. The last review is by F. E. Russell on the poisons of marine animals. It is an attractive review on the history, anatomy, toxicology, and clinical problems of fish poisons and others.

Illustrations and tables are clear, but the subject index is rather short.

D. H. Cushing

ENTOMOLOGY

Radioisotopes and Ionizing Radiations in Entomology, *Vol. II* (1961–1963). *(Bibliographical Series No. 15), compiled by M. Binggeli. Pp. 564. International Atomic Energy Agency, Vienna. 1965. 66s.*

The greater number of published papers embraced by the present triennial review compared with that of the preceding decennial one is a startling indication of the explosive growth in the biological applications of radioisotope techniques. An introduction that critically discusses the ways in which radioisotopes and their radiations are used for entomological

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research and insect control is followed by 1585 abstracts of research papers and review articles, arranged according to subject of investigation and in two parts—radioisotopes, and ionizing radiations. A final section of the abstracts deals specifically with research and analytical techniques and makes reference to earlier abstracts in the same context. Two tables summarize data on the dispersion of tagged insects, and the doses required for the irradiation sterilization of the many different species that have now been studied. Subject and author indexes, the latter usefully including the authors' locations, complete the volume. The bibliography represents a painstaking and intelligent undertaking by its compiler, Dr Marlene Binggeli. However, its size is due to the diversity of applications of essentially similar techniques, and this prompts one to question the usefulness of continuing the series in its present form. The need for international documentation and coordination in this area is unquestioned, but a future emphasis on essentially new techniques and methodology would now seem to be indicated. The volumes to date provide a unique reference source for all who are concerned with the use of radioisotopes or their radiations in entomology. *F. P. W. Winteringham*

ANALGETICS

Analgetics, edited by George deStevens. *Pp. xiii+475. Academic Press, New York. 1965. 136s.*

This book contains eight chapters by fifteen authors, the majority of whom are scientists in pharmaceutical companies. Several of the authors have played important parts in the recent development of analgetic drugs. Perhaps the most impressive of these developments concerns addictiveness. All of the earlier analgetics of the general group of morphine induce dependence with a potency roughly equal to that with which they suppress pain. The observation, made in the 1950s, that the morphine relative and antagonist, nalorphine, had analgetic action in man, without evident addictiveness, showed that this association could be broken. The resulting development of the benzo-morphans, in some of which analgetic and addictive activities are quite disconnected, is described in the chapter by E. L. May and L. J. Sargent, which thoroughly covers the development of phenazocine; however, it deals more sketchily with pentazocine and cyclazocine, in which separation of the two activities is more pronounced.

The new trend represented by the benzomorphans has been made possible by methods of measuring two effects of analgetic drugs—one, the relief of natural, as distinct from experimental, pain in man; and the other, the induction of drug-dependence. The former method, which in turn is based on recognition of the 'placebo effect', is satisfactorily covered in the chapter by R. W. Houde, S. L. Wallenstein, and W. T. Beaver. Methods of measuring the capacity to induce dependence, however, are not fully dealt with in this book, although briefly discussed in the interesting chapter by C. A. Winter.

Most of the rest of the book contains well documented accounts of the development of particular chemical groups of analgetics. The fact that industrious research has produced some drugs of enormous potency, with probably equal powers of addiction and corresponding social menace, emphasizes the importance of the work separating addictive from analgetic activity. *H. O. J. Collier*

HISTORY OF SCIENCE

Joseph Priestley, Adventurer in Science and Champion of Truth, *by F. W. Gibbs. Pp. xii+258. Thomas Nelson and Sons, Edinburgh. 1965. 42s.*

This excellent book, well written, well illustrated, and the work of a mature historian of science, covers in a reasonable compass every aspect of the life of Joseph Priestley who was one of the outstanding figures of eighteenth-century England. It completely eclipses the earlier biographies of Thorpe and Holt, each of whom tended to present an unevenly balanced account of their subject's multifarious activities. It is, of course, no easy task to write a life of Priestley, who was a Dissenting minister, tutor, schoolmaster, grammarian, educationist, historian, theologian, physicist and, above all, chemist; moreover, he was an outstanding author on an almost heroic scale and prominently involved in every national debate where he considered truth, freedom, and intellectual honesty to be at stake. Dr Gibbs has succeeded admirably, and a vivid and living personality emerges from his pages; it is sad that his recent untimely death deprives us of further works of such quality from his pen. He writes of Priestley's ancestry and his early ill-health, both important factors in moulding his mind and character—and of his studies in Daventry Academy, his early pastorates, his life in Warrington and in Leeds, his association with Lord Shelburne, and his later years in Birmingham and Hackney and in America. The chapters on his scientific work give the best critical account so far available. *Douglas McKie*

HISTORY OF TECHNOLOGY

Science and Civilization in China, *Vol. IV, Part 2,* Mechanical Engineering, *by Joseph Needham. Pp. xxxiv+759. Cambridge University Press. 1965. 190s.*

Physical theories and deductive geometry did not develop in China, but this did not preclude the remarkable technological achievements that are discussed in the latest part of this massive work. It shows that a great variety of machinery was used in ancient and medieval China, where it seems to have encountered less opposition from craftsmen fearing unemployment than in Europe.

Dr Needham does not consider Chinese civilization in isolation, and he is largely concerned with the mutual influence of East and West. Reference is made to archaeological discoveries from many parts of Europe and Asia; illustrated books provide information about engineering practice from the eleventh to the eighteenth centuries; and for recent developments Dr Needham is able to draw on his own observations, for he has travelled extensively in China. His 'balance-sheet' shows that the Archimedean screw, the crankshaft and other inventions moved from West to East, but that Europe was indebted to China for many fundamental innovations, including the collar-harness that greatly improved the efficiency of the horse. An important feature of Chinese technology was the use of water-power; textile machinery, for example, was driven by water in the thirteenth century, at least 300 years earlier than in Europe.

This thoroughly documented book is an indispensable work of reference for historians of science and technology; it is lucidly written and very well illustrated and can also be recommended to the non-specialist. The appearance of the next part, dealing with civil and hydraulic engineering and marine technology, is eagerly awaited. *W. A. Smeaton*

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Some books received

(*Note.* Mention of a book on this page does not preclude subsequent review.)

MATHEMATICS

Elementary Abstract Algebra, *by E. M. Patterson and D. E. Rutherford. Pp. viii+211. Oliver and Boyd, Edinburgh. 1965. 17s. 6d.*

Mathematics for Quantum Chemistry, *by J. M. Anderson. Pp. x+154. W. A. Benjamin, New York. 1966. $6.*

Plateau's Problem: An Invitation to Varifold Geometry, *by F. J. Almgren, Jr. Pp. xii+74. W. A. Benjamin, New York. 1966. $4.95.*

ASTRONOMY

Sternglaube, Sterndeutung, Sternkunde, *by F. Baur. Pp. 140. Josef Knecht, Frankfurt. 1965. 6.80 DM.*

PHYSICS

Esprit et bon usage du système métrique, *by M. Danloux-Dumesnils. Pp. 190. Dunod, Paris. 1965. 12 F.*

The Gaseous State, *by N. G. Parsonage. Pp. xiv+170. Pergamon Press, Oxford. 1966. 18s. 6d.*

Lie Groups for Physicists, *by R. Hermann. Pp. vii+193. W. A. Benjamin, New York. 1966. $13.75.*

Matière, rayonnement, énergie, *by U. Filippi. Pp. xvii+289. Dunod, Paris. 1966. 19 F.*

Molecules, Crystals, and Quantum Statistics, *by E. Fermi (translated from the Italian by M. Ferro-Luzzi and edited by L. Motz). Pp. xiv+300. W. A. Benjamin, New York. 1966. $13.50.*

Optical Pumping: An Introduction, *by R. A. Bernheim. Pp. xi+272. W. A. Benjamin, New York. 1965. Cloth, $9.90; paper, $5.54.*

Symmetry Groups in Nuclear and Particle Physics, *by F. J. Dyson. Pp. xii+320. W. A. Benjamin, New York. 1966. $10.*

The Theory of the Microscope, *by L. C. Martin. Pp. xiv+488. Blackie and Son, London. 1966. 100s.*

Thermodynamics of Certain Refractory Compounds, *Vol. I,* Discussion of Theoretical Studies, *edited by H. L. Schick. Pp. iii+632. Academic Press, New York. 1966. 168s.*

CHEMISTRY

The Analytical Chemistry of Cobalt, *by R. S. Young. Pp. vii+171. Pergamon Press, Oxford. 1966. 45s.*

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